An adiabatic calorimeter for heat capacity measurements in the temperature range 300–600 K and pressure range 0.1–15 MPa [a]

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(Received 30 July 1990)

Abstract

An adiabatic high pressure calorimeter for heat capacity measurement was constructed. The shape of the calorimeter cell was nearly spherical to minimize the cell mass relative to the volume of the sample chamber. The cell was made of stainless steel which is resistant to corrosion by the reactive specimens and has sufficient mechanical strength to withstand the applied pressure. The pressure in the cell was controlled by joining the cell through a transmitting tube to a stabilized highly pressure system in which nitrogen gas was used as the pressure-transmitting medium. The adiabatic conditions were achieved by controlling the temperature of the adiabatic shields surrounding the cell and the tube, and evacuating the space of the thermostat housing the cell. The apparatus is capable of heat capacity measurement under constant pressure from 0.1 to 15 MPa and over the temperature range from 300 to 600 K. The results of heat capacity measurements of liquid water and crystalline α-Al_2O_3 demonstrated that the colorimeter has an accuracy of 0.5% for both liquid and solid samples.

INTRODUCTION

The heat capacity of a substance is an important thermodynamic property and has significance not only for practical applications but also for basic science. Heat capacities of various substances have hitherto been measured with high precision and accuracy over a wide temperature range at atmospheric pressure. However, few quantitative measurements of heat capacity under pressure have been reported so far, although a number of physico-chemical phenomena are most profitably studied by detailed and accurate measurement of the heat capacity as a function of both temperature and pressure. The development of heat capacity measurements under pressure is

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[a] Presented at the Second Japan–China Joint Symposium on Calorimetry and Thermal Analysis, 30 May–1 June 1990, Osaka, Japan.
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naturally expected to contribute significantly to the further understanding of the behaviour of substances at normal pressure as well as under pressure.

The heat capacity of condensed matter is usually measured under constant pressure because of the difficulty in keeping the volume of the specimen constant. At ordinary pressures and low temperature, adiabatic calorimetry is widely used as the most reliable method for obtaining accurate heat capacity data. However, the extension of this method to elevated pressures and temperatures is not straightforward owing to many technical difficulties. One of these problems originates from the increase in the mass of the calorimeter cell used for maintaining the high pressure. An increase in the mass of the cell leads to a decrease in the ratio of the sample heat capacity to the total observed heat capacity which casts doubt on the certainty of the measurement. The heat capacity of a sample under study is, as a rule, only a small part of that of the cell. This brings about a corresponding decrease in the accuracy of measurement. Another difficulty is to find materials suitable for constructing the calorimeter vessel, which must have sufficient mechanical strength to withstand the required pressure. Other calorimetric components, including lead wires, enamel, heater, thermometer etc., must have good electrical insulation capability and thermal stability at elevated temperatures.

Two set-ups for measuring heat capacity under high pressure by adiabatic calorimetry are possible, depending on whether the pressurized specimen is isolated from the surroundings or is in contact with an external pressure reservoir. The former condition is realized in a clamp-bomb calorimeter in which the high pressure is generated and clamped by means of a screw situated in the thermostat. In this calorimeter the actual pressure that the sample experiences during a heat capacity measurement changes in a manner too complex to be described properly owing to the volume change of the substance in the calorimeter cell. Hence it is unsuitable for the study of liquids and of those solids which undergo phase transitions when the temperature changes. The latter alternative is achieved by joining the calorimeter cell to an external pressure-control system with a pressure-transmitting tube. In such a calorimeter, transfer of a part of the pressure medium out of or into the cell is inevitable as the temperature of the cell changes.

On the basis of our previous work [1] and on that of other investigators [2,3], we have constructed a moderately high temperature and constant high pressure adiabatic calorimeter for heat capacity measurements in the temperature range 300–600 K and the pressure range 0.1–15 MPa. The results of heat capacity measurements on liquid water and crystalline $\alpha\text{-Al}_2\text{O}_3$ have proved that this calorimeter has an accuracy of 0.5% in the above temperature and pressure ranges for both liquid and solid specimens.

This apparatus has been applied mainly to materials associated with petroleum geology, including natural oils, underground waters, oil sands,

clays etc., to determine accurately the heat capacities of various natural oil-sand core samples under simulated in situ conditions. The main purpose of this research project is to provide sufficient and reliable fundamental thermal data for a feasibility study on the thermal stimulation scheme of exploitation of the natural heavy oil reservoir in the Liaohe Oilfield, in north-east China.

EXPERIMENTAL

Construction of the calorimeter

Figure 1 is a schematic drawing of the calorimeter and thermostat assembly. The calorimeter cell M is made of stainless steel (1Cr–18Ni–9Ti)
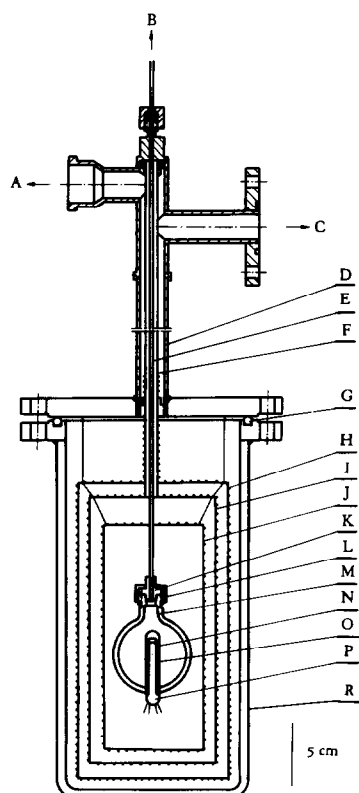

Fig. 1. Schematic drawing of the adiabatic calorimeter: A, to calorimetric system; B, to high pressure system; C, to vacuum system; D, stainless steel tube for evacuation and drawing out the lead wires; E, pressure-transmitting tube; F, shield for the pressure-transmitting tube; G, fuse O-ring gasket; H, outer radiation shield; I, middle guard shield; J, inner adiabatic shield; K, brass cone core; L, gland nut; M, calorimeter cell; N, central re-entrant well; O, calorimeter heater; P, platinum resistance thermometer; R, stainless steel vacuum can.

which is corrosion resistant to the specimens to be studied and has sufficient mechanical strength to withstand the applied pressure. Pressure sealing is established by a brass cone core K and a stainless steel gland nut L. The maximum pressure applied without breaking, tested in a high pressure hydraulic system, was about 35 MPa at 600 K. The nearly spherical shape of the cell was devised in order to minimize the mass of the empty cell and to maximize the space of the sample chamber. This design helps to increase the ratio of the sample heat capacity to the total heat capacity, and consequently contributes to an improvement in the precision of the heat capacity measurement. The volume of the sample chamber is 26.806 cm^3 at 293 K and the mass of the empty cell is around 200 g.

The calorimeter cell is equipped with a platinum thermometer P, Model PT4-20 (Guangmin Co., People's Republic of China), and a heater O (Teflon-insulated Karma wires, about 100 Ω). The thermometer–heater assembly is located at the central entrant well N of the cell. The platinum resistance thermometer was calibrated at the National Institute of Metrology (NIM) in terms of IPTS-68: $R_0 = 21.8439 \; \Omega$, $W_{100} = 1.39267$, $W_{Zn} = 2.56819$.

At the top of the calorimeter cell, an inlet of 5 mm inner diameter is provided for admitting liquid and solid samples.

The calorimeter cell is surrounded in turn by three shields designated the inner adiabatic shield, the middle guard shield and the outer radiation shield respectively. All the shields are made of 0.5 mm sheet copper and manganin heating wires were wound on their peripheries to control the shield temperatures. The outer surfaces of these shields over the heating wires are covered with highly polished aluminium foil so as to diminish thermal radiation. Three sets of 4-junction chromel–copel(Ni, 55%; Cu, 45%) differential thermocouples were installed between the calorimeter cell and the inner adiabatic shield, between the adiabatic shield and the guard shield, and between the guard shield and the outer radiation shield, in order to sense the respective temperature differences. All the wires, including the heating wires and the electrical lead wires, are insulated with double glass-fibre wrap, cemented with polyimide lacquer and finally wrapped with Teflon film to improve the electrical insulation and mechanical strength. The lead wires which come from the thermometer–heater assembly are attached in turn to the adiabatic shield, the guard shield and the radiation shield so as to obtain good temperature control. A vacuum can R houses the calorimeter cell and shields in a high vacuum space in which a vacuum of 10^{-4} Pa can be maintained during the heat capacity measurements.

High pressure system

The high pressure system consists of four parts for the generation, transmission, measurement and control of the pressure. High pressure is

generated by compressing nitrogen gas supplied from a steel tank with a compressor. A pressure-transmitting capillary tube E (0.5 mm outer diameter ×0.3 mm inner diameter), made of stainless steel, enters the calorimeter cell from the external pressurization system. Nitrogen gas, used as the pressure-transmitting medium, flows into or out of the cell through the tube and maintains the pressure inside the cell at a constant value. Pressure control was realized by using a large capacity steel bottle as the pressure buffer, which is about 100 times larger (4 dm^3) than the calorimeter cell and is placed inside a thermostat controlled at $20 \pm 0.1\,^\circ$C. This is sufficient to compensate for the pressure increase due to the temperature rise of the calorimeter cell during the calorimetric measurements over 300–600 K. The pressure inside the cell is measured and read from a standard digital gauge with a precision of 0.05 MPa. The pressure can be maintained constant within 0.1 MPa over the entire pressure and temperature ranges.

Calorimetric measurement system

Heat capacity measurements are carried out in the standard fashion. Figure 2 shows the block diagram of the whole measurement system. The temperature of the calorimeter cell is determined by measuring the resistance of the platinum thermometer installed in the cell using a high precision integrating digital multimeter (Model 6030, Sabtronics, Co., Switzerland). This resistance is converted to a temperature using the previously calibrated IPTS-68 function. The resolution of the temperature measurement circuit was estimated to be about 0.1 mK.
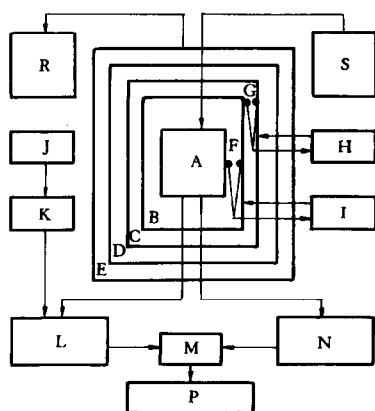

Fig. 2. Block diagram of the entire calorimetric system: A, calorimeter cell; B, C, D, inner, middle, outer shield; E, vacuum can; F, G, differential thermocouples; L, energy measurement circuit; M, interface; N, temperature measurement circuit; P, computer; R, vacuum system; S, high pressure system.

The electrical energy introduced into the calorimeter cell is supplied by a constant-current power supply, Model HT-1721C (Shijiozhuang R.M. Co., People's Republic of China), with a stability of 5 ppm. The energy supplied is determined from the observed potential drops across the calorimeter heater and the standard resistor (100 Ω) connected in series with the heater, and from the recorded duration of energy input. The potential drops are measured using the same digital multimeter mentioned above. The heating interval is controlled and measured by a digital display electronic timer–controller, Model JK-1, (DICP Products, People's Republic of China), which is placed in the energy measurement circuit and has a measuring error of 1 ms.

A personal computer P (Model IBM-PC/AT-286, U.S.A.) was used for the automatic data acquisition system. The temperature and energy measurements, the calculation to obtain the molar heat capacity of the sample and the data storage were all performed on the computer.

Automatic adiabatic control system for the calorimeter cell

Adiabatic conditions in the calorimeter cell are achieved by the conventional method: evacuating the space inside the vacuum thermostat and automatically controlling the innermost adiabatic shield and the pressure-transmitting tube at the same temperature as the cell.

Four similar feedback circuits are used to control the temperature of the inner, middle, outer and tube shields. Each circuit consists of a chromel-to-copel thermocouple mounted on the shield, a microvolt amplifier, a recorder, an ACD-79 three-action controller, a power amplifier and the shield heater. For each temperature-control channel the signal from the differential thermocouple is greatly amplified by the DWT-702 microvolt amplifier. The amplified signal is monitored by the recorder and transferred to the ACD-79 controller which provides for proportional, integral and differential (PID) control. The output of the controller in turn controls the output potential of the power amplifier to deliver a corresponding current to the shield heater. By using the control circuit the difference in temperature between the calorimeter cell and the adiabatic shield can usually be kept to within 5 mK during the heating period and to within 0.5 mK during the equilibration period, whereas the observed temperature drift rate of the calorimeter cell is lower than 0.1 mK min^{-1} during the drift period.

Experimental procedures

The operation details of this apparatus are similar to those given in ref. 1 for adiabatic heat capacity measurement at normal pressure. After the calorimeter cell had been charged with the sample to be measured, the cell was attached to the high pressure system through the pressure-transmitting

tube and sealed tightly by screwing down the gland nut at the top of the cell. The required pressure of nitrogen gas for the measurement was applied to the sample by adjusting the pressure control system. After the whole calorimetric system had been assembled, the thermostat was evacuated to about 10^{-3} Pa and the adiabatic control system was activated. Thereafter, calorimetric measurements were carried out in the standard fashion.

The heat capacity measurements were performed as a function of temperature using the standard discontinuous heating method. In this intermittent mode, the sequence of each heat capacity measurement is composed of two alternating periods. One is called the drift period during which the temperature of the sample cell is observed as a function of time. The other is called the energy input period during which a definite amount of electrical energy is supplied to the calorimeter cell. We were especially careful to allow the calorimeter and contents to reach thermal equilibrium after each energy increment. This occurred within 30–45 min after the energy input, but might take as long as several hours if the sample in the calorimeter was undergoing a transition process. The heat input–equilibration cycle was repeated until the upper limit of temperature for the measurements, about 600 K, was reached. A separate series of heat capacity measurements on the empty cell was carried out before the measurements on the charged cell. The heat capacity of the sample was obtained from the two series of measurements with corrections for any differences in the heat capacity of the cell when filled and when empty.

RESULTS AND DISCUSSION

To verify the reliability of this calorimeter for heat capacity measurements on both liquids and solids, measurements were made on two standard reference substances, liquid water and crystalline α-Al_2O_3, in the temperature range 300–600 K and under 0.1–12 MPa pressure.

The water sample used for the measurement was redistilled and degassed carefully before introduction into the calorimeter cell. The mass of the sample loaded in the cell was 19.1068 g.

The α-Al_2O_3 specimen, purchased from No. 1 Reagent Co., Shanghai, People's Republic of China, was a spectroscopically pure reagent of 99.993 wt.% purity. The spectroscopic analysis showed that the sample contained the following impurities (wt.%): Fe, 0.001; Mg, 0.002; Si, 0.003; Ca, 0.001. The sample was calcined at 1900 K for 2 h. The powder X-ray diffraction results showed that the whole sample was in the α phase after the treatment. The mass of the sample loaded into the calorimeter cell was 35.4837 g.

The heat capacities of the empty cell were measured at 0.1 MPa and 12 MPa; the range of values was about 110–130 J K^{-1} between 300 and 600 K. One series of measurements on water was made at 12 MPa. Two series of

TABLE 1

Experimental molar heat capacity of liquid water: $M(H_2O) = 18.016$ g mol^{-1}, $p = 12.0$ MPa

T (K)	C_p (J K mol^{-1})	T (K)	C_p (J K mol^{-1})	T (K)	C_p (J K mol^{-1})
290.73	74.73	391.29	75.79	492.86	81.74
296.62	74.71	397.48	75.96	499.11	82.37
302.42	74.69	403.64	76.15	505.28	83.11
308.25	74.67	409.77	76.39	511.39	83.92
314.06	74.69	415.85	76.64	517.42	84.80
319.86	74.71	421.90	76.89	523.41	85.81
324.77	74.80	427.90	77.18	528.87	86.73
330.47	74.82	433.84	77.47	531.24	87.38
336.17	74.86	439.75	77.75	537.46	88.58
341.85	74.91	441.84	77.88	543.26	89.99
347.34	74.98	447.72	78.24	549.36	91.56
352.99	75.04	453.52	78.55	555.35	93.74
358.63	75.09	457.69	78.80	559.56	95.32
364.28	75.22	464.30	79.16	565.78	97.74
367.45	75.33	470.21	79.63	571.22	99.98
373.17	75.43	476.65	80.21	576.24	102.64
379.23	75.52	483.01	80.76	580.18	104.76
385.49	75.69	486.60	81.14		

measurements on α-Al$_2$O$_3$ were made at 0.1 and 12 MPa. The heat capacity of the samples was obtained as the difference between the heat capacities of the loaded and empty cell. All measurements were performed at the heating rate of about 0.5 K min^{-1}; the experimental temperature increment over the entire temperature range was about 5 K for each measurement, as might be inferred from adjacent mean temperatures. The experimental results for water and α-Al$_2$O$_3$ are given in chronological order in Tables 1 and 2 respectively.

We have assessed the accuracy of this apparatus by comparing our data with recommended literature values [4–6]. The average differences between our results and the commonly accepted values are 0.52% for water and 0.44% for α-Al$_2$O$_3$. From the test results it could be concluded that the inaccuracy of the present calorimeter for heat capacity measurements on both liquids and solids is approximately 0.5% in the ranges 300–600 K and 0.1–15 MPa.

Adiabatic high pressure calorimetry has the inevitable disadvantage that the heat capacity of the empty cell is much larger than that of the sample. In the present calorimeter the value at 300 K is about 110 J K^{-1} which is five times larger than that of a typical sample. Considering that the heat capacities of the empty cell and the sample are generally comparable in magnitude in conventional adiabatic calorimeters, the precision of the heat capacity data obtained in our calorimeter would be five times poorer than

TABLE 2

Experimental molar heat capacity of α-Al$_2$O$_3$: $M(\text{Al}_2\text{O}_3) = 101.9613$ g mol^{-1}

T (K)	C_p (J K mol^{-1})	T (K)	C_p (J K mol^{-1})	T (K)	C_p (J K mol^{-1})
		486.69	104.88	375.09	92.61
$p = 0.101$ MPa		492.62	105.34	380.82	93.46
286.80	76.44	498.65	105.83	386.75	94.22
292.78	77.79	504.81	106.37	392.24	94.98
298.86	79.05	511.07	106.82	399.37	95.87
303.78	80.13	518.97	107.41	406.27	96.66
311.26	81.73	525.41	108.01	412.93	97.51
317.39	83.04	531.52	108.53	419.89	98.29
323.49	84.17	537.56	108.99	426.33	99.01
330.60	85.51	543.89	109.45	431.41	99.51
335.12	86.37	549.82	109.83	436.61	100.06
340.26	87.23	555.78	110.22	442.29	100.71
346.33	88.17	561.04	110.51	448.32	101.32
352.17	89.12	567.77	110.89	455.99	102.08
358.63	89.97	573.04	111.28	462.42	102.76
365.06	91.29	577.92	111.59	468.97	103.43
371.45	92.21	582.61	111.91	475.63	104.00
376.12	92.92	588.57	112.24	481.82	104.54
383.82	94.01			487.79	105.09
390.03	94.92	$p = 12.0$ MPa		493.63	105.61
396.24	95.63	588.57	76.25	500.61	106.23
403.27	96.47	294.83	78.25	506.98	106.72
410.71	97.36	301.59	79.65	513.08	107.17
417.07	98.05	306.07	80.66	519.49	107.63
423.54	98.73	311.78	82.01	525.84	108.14
429.61	99.36	317.99	83.23	532.13	108.58
435.02	99.97	323.56	84.27	538.37	108.99
441.98	100.68	329.54	85.35	544.39	109.42
448.14	101.27	335.11	86.42	550.63	109.85
453.93	101.88	340.07	87.24	556.11	110.15
460.23	102.44	345.37	88.04	562.35	110.54
466.84	103.09	351.01	88.96	569.62	110.98
473.23	103.69	356.12	89.69	576.02	111.43
480.13	104.34	362.52	90.81	582.09	111.79
		369.06	91.79	588.53	112.22

that of the ordinary calorimeter (i.e. below 0.5%). The actual precision estimated from the test measurements on water and α-Al$_2$O$_3$ is indeed in agreement with this value.

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