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Measurement of isobaric heat capacity of pure water up to supercritical conditions

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ABSTRACT

A flow calorimeter was developed to measure the isobaric heat capacities of pure water at high pressure and high temperature up to supercritical region. Experimental isobaric heat capacities of pure water from 395 K to 665 K and pressure up to 26 MPa are presented. The total measurement uncertainties of temperature and pressure were ±0.02 K and ±3.88 kPa, respectively. The relative uncertainty of the isobaric heat capacity was estimated to be ±0.98%. The aim of this study is to provide new experimental data to complete the non-experimental data region and to check the accuracy of the IAPWS-95 formulation. The IAPWS-95 formulation shows great accuracy at temperatures under 623 K and at pressures under 22 MPa region. However, in the near-critical and supercritical region, its accuracy needs more experimental data for verification and to extend theories.

1. Introduction

Of all pure engineering fluids, water is the most important substance in existence [1]. Reliable experimental heat capacities data are required for designing the steam power cycles which supply electricity in large amounts to the industrialized world, the water heat exchanger [2] and chemical systems [3], especially at high temperature and high pressure condition.

A release on the IAPWS-95 formulation [4] for the thermodynamic properties of ordinary water substance has been issued by the International Association for the Properties of Water and Steam in 1995, which is generally accepted as reliable for calculating the isobaric heat capacity of pure water by the scientific community. However, in that work, nearly all the data for the isobaric heat capacity of pure water are based on measurements of Sirota's group [5,6] in the period from 1956 to 1970. Since then, only three further c_p data sets reported by Angell et al. [7], Czarnota [8], Archer and Carter [9] have been used for fitting the IAPWS-95 formulation, as shown in Fig. 1 [4].

In addition, Chen [10] reported the c_p data for water at temperatures of 273.15 K and 373.15 K and pressure of 100 MPa in 1987; Ernst and Philippi [11] presented the c_p data at temperatures from T = (298–673) K and pressures from p = (20–50) MPa in 1990; Wiryana et al. [12] reported c_p data for temperatures from T = (353.15–473.15) K and pressures from p = (250–3500) MPa in 1998; Manya et al. [13] reported the c_p data for water at temperatures from T = (298.15–465.65) K at 0.1 MPa and 4 MPa in 2012; Zheng et al. [14] reported the c_p data for water at temperatures from T = (294–353) K and pressures from p = (0.1–15) MPa in 2014, as shown in Fig. 2. Figs. 1 and 2 show that the c_p data in some region are still scare, such as the region at temperatures from T = (350–620) K and pressures from p = (5–20) MPa.

On the other hand, IAPWS-95 formulation is not in good agreement with the data in the work of Ernst and Philippi [11] and Manya et al. [13]. Fig. 3 shows that the data presented by Manya's group [13] in 2011 for the specific heat capacity of pure water were in disagreement with the values calculated from the IAPWS-95 formulation, especially at high temperature and high pressure, where the deviation is up to 27.2%; in the near critical region, the deviation between the specific heat capacity data reported by Ernst's group [11] in 1990 and the values calculated from the IAPWS-95 formulation is up to 98%.

Therefore, new reliable experimental data for isobaric heat capacity of pure water are necessary to complete the non-experimental data region and to improve the accuracy of the IAPWS-95 formulation. In this work, we develop a flow calorimeter to measure the isobaric heat capacity of pure water at high pressure and high temperature. In the near critical region, gravity can result in vertical density floor. The pipeline in the experimental cell is installed in a horizontal position to reduce the influence of gravity. We present isobaric heat capacities of pure water in the temperature range from T = (395–665) K and pressure up to 26 MPa.

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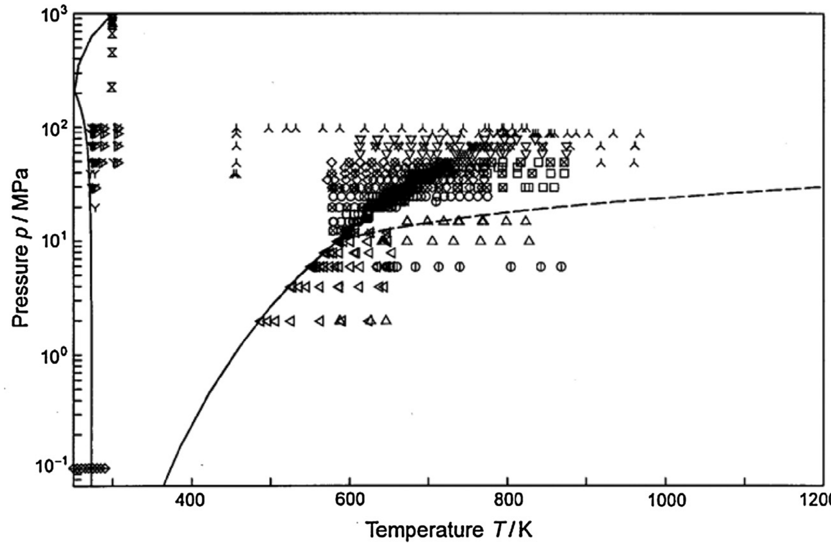

Fig. 1. Published experimental c_p data region used for fitting the IAPWS-95 formulation [4]. ◁ Sirota and Timrot (1956), △ Sirota (1958), ◇ Sirota and Maltsev (1959), □ Sirota and Maltsev (1960), ⦶ Sirota and Maltsev (1962a), ○ Sirota and Maltsev (1962b), ▽ Sitota et al. (1963), × Sitota et al. (1966), ⅄ Sitota and Grishkov (1966), ▷ Sitota and Grishkov (1966), Y Sitota et al. (1970), ⬘ Angell et al. (1982), ⧗ Czarnota (1984), — Phase boundaries, — Isochore ρ = 55 kg·m^{-3}.

2. Experiment

2.1. Apparatus

The isobaric heat capacity of pure water was measured using a high pressure and high temperature flow calorimeter which has been described in our former publication [15]. The main apparatus used in the present measurements is schematically shown in Fig. 4.

At the beginning of the experiment, water was allowed to flow through the experimental cell, and its pressure was regulated by a plunger-type pump (Scientific Systems, Series 1500 HPLC Pump) and a back-pressure valve. Then, the effluent flowed into a container for waste after the pressure and the temperature was reduced. When the flow was stable, fluid flowed into the container for measurement by switching the three way valve and then timed by a stopwatch with an uncertainty less than 0.001 s. The flow was regulated by a plunger-type pump and mass was checked. The mass of fluid in the container for measurement was measured with an analytical balance (ME204, METTLER TOLEDO) with an uncertainty of 0.1 mg. The pressure of the experimental cell was measured by two absolute pressure transmitters (Rosemount, 3051S).

The experimental cell consisted of heaters, thermometers and vacuum cylinders as shown in Fig. 5(a) and (b). To reduce the heat loss, a double layer vacuum cylinder was used and fluid was heated by a microheater inside the tube assembly. Temperature in the experimental cell was controlled by two electrical heaters and four platinum resistant thermometers (PRT) purchased from Fluke Corporation with an uncertainty of ±0.02 K (k = 2). Two thermometers were inserted into the copper blocks to measure the temperature of fluid before and after heating. Two PRTs were located in the vacuum cylinder to minimize the inhomogeneities of temperature.

In the near-critical regions, vertical density stratification will be produced because of gravity. To reduce the influence of gravity, the pipeline in the experimental cell is in a horizontal position, which is different from the traditional flow calorimeter [16,17].

2.2. Work equation

For flow calorimeters, the isobaric heat capacity c_p of fluid at a fixed pressure p can be calculated by [16–18]:

$$c_p(T,p) = \frac{P}{q_m \cdot \Delta T} = \frac{P}{q_m \cdot (T_2 - T_1)} \quad (1)$$

where q_m is the mass flow of fluid through the calorimeter; P is the heat flow obtained from the heater; T_1 and T_2 are the inlet and outlet

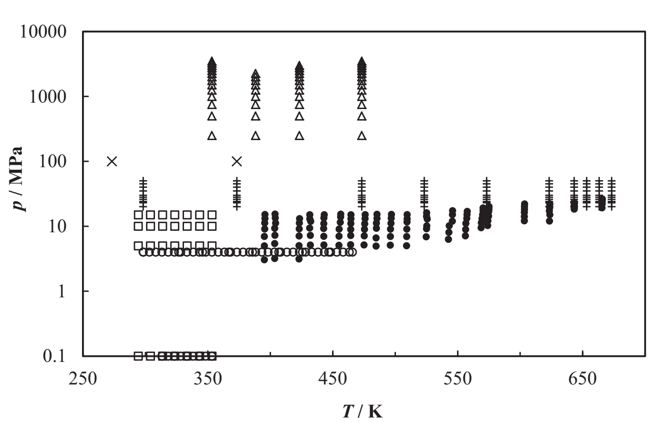

Fig. 2. Recent experimental data in literatures. × Chen [10], + Ernst and Philippi [11], □ Wiryana et al. [12], ○ Manya et al. [13], □ Zheng et al. [14], ● This work.

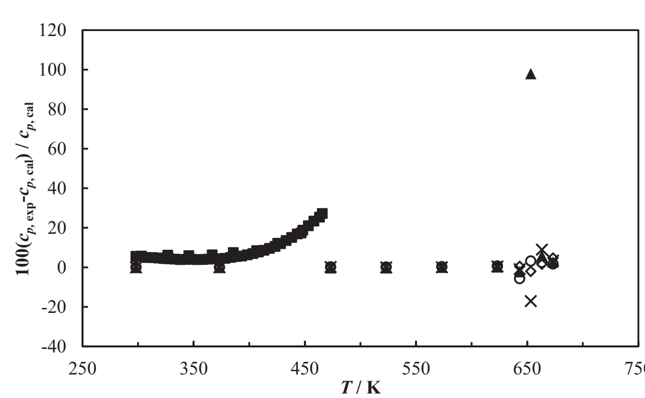

Fig. 3. Comparison of experimental data with calculation values from IAPWS-95 formulation [4]. ■ Manya et al., 4 MPa [13], ○ Ernst and Philippi 20 MPa [11], ▲ Ernst and Philippi 23 MPa [11], × Ernst and Philippi 24 MPa [11], ◇ Ernst and Philippi 26 MPa [11].