

New Apparatus for Measurements of Isobaric Heat Capacity for Aqueous Fluids at High Temperatures and Pressures

Katsuyuki Tanaka* and Masahiko Uematsu

Center for Mechanical Engineering and Applied Mechanics, Keio University,
Yokohama 223-8522, Japan

*E-mail: tanaka_katsuyuki@hotmail.com

We have developed a new calorimeter for measurements of isobaric specific heat capacity for aqueous mixtures at high temperatures and pressures. Principle for analysis of isobaric specific heat capacity is based on the lumped system analysis. Calorimeter is designed so as to satisfy the principle under the specification for fluids at high temperatures and pressures. Calorimeter with a metal-bellows is assembled in a pressure vessel and surrounded by nitrogen gas whose pressure kept constant. A heater for supplying heat flow at a constant rate is installed in the lowest part of the calorimeter which is equipped with five thermometers for measuring temperature and its distribution of the sample. Pressure vessel is immersed in a thermostatted oil bath whose temperature kept constant. It is confirmed that this calorimeter satisfies the criteria for lumped system by the result of the temperature distribution and behavior of heating curves. Specific heat capacity of the sample is obtained from the relaxation time measurements with known mass of the sample loaded into the calorimeter, when apparatus constants of thermal conductance and the heat capacity of the sample container are calibrated. Water and toluene are used as a calibration fluid to determine thermal conductance and heat capacity of the sample container. The performance of this calorimeter is confirmed by measuring the isobaric specific heat capacity of methanol at 323.15 K and 0.1 MPa.

1. Introduction

We have developed a new calorimeter by using metal-bellows as a sample container based on the heat relaxation method for measurements of isobaric heat capacity for aqueous fluids at high temperatures and pressures.

2. Principle

Consider a closed system consisted of a sample container and a fluid sample as shown in Fig.1. When the system is heated by a heater in it, its temperature increases with growing temperature distribution and the remaining heat flows to the surroundings. However, assuming thermal resistance inside the system is sufficiently less than that of the surface of the system, we can consider that the temperature distribution throughout the system is practically uniform. This system is called as lumped system and its temperature history can be taken to be a function of time only. When the system is set in a constant temperature T_0 field and

heated with a constant heat flow rate \dot{Q} , the balance equation of the system for energy E is written as

$$\frac{dE}{dt} = \dot{Q} - \dot{Q}_L \quad (1)$$

Here, \dot{Q}_L is heat flow rate from the system to the surroundings and is proportional to the temperature difference $\Delta T = T - T_0$ and the surface area A of the system.

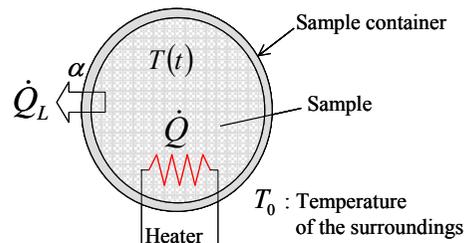


Fig. 1. Schematic structure of the system.

$$\dot{Q}_L = hA\Delta T = hA(T - T_0) \quad (2)$$

Here, h is heat transfer coefficient and T is temperature of the system. Introducing heat capacity C of the system, equation (1) can be reduced as

$$\frac{dE}{dt} = C \frac{dT}{dt} = \dot{Q} - \dot{Q}_L. \quad (3)$$

Substituting Eq. (2) into Eq. (3) yields

$$C \frac{dT}{dt} = \dot{Q} - hA(T - T_0). \quad (4)$$

When \dot{Q} becomes balanced with \dot{Q}_L , temperature of the system reaches to a maximum T_{\max} and equation (4) can be written

$$0 = \dot{Q} - hA(T_{\max} - T_0). \quad (5)$$

Substituting Eq. (5) into Eq. (4) yields

$$\frac{dT}{dt} = -\frac{hA}{C}(T - T_{\max}) \quad (6)$$

Assuming h and A are constant, Eq. (6) can be integrated with an initial condition $T = T_0$ at $t = 0$.

$$\Delta T = T - T_0 = (T_{\max} - T_0) \left[1 - \exp\left(-\frac{hA}{C}t\right) \right] \quad (7)$$

The product hA is heat conductance α and time constant τ called relaxation time is expressed by Eq. (9).

$$hA = \alpha \quad (8)$$

$$\tau = \frac{C}{\alpha} \quad (9)$$

It takes longer for the system to reach equilibrium with the surroundings when the heat capacity C is larger and/or heat conductance α is smaller. Since the system is consisted of the sample container and fluid sample, the heat capacity C of the system can be written

$$C = mc + C_a, \quad (10)$$

where the product mc is a heat capacity of the sample with its mass m and C_a is heat capacity of the sample container.

Prior to the measurements, apparatus constants α and C_a should be calibrated. During the system is heated, temperature of the system is measured at a certain time interval. Based on these measurements, relaxation time τ is determined by fitting to Eq. (7) and heat capacity of the sample mc can be calculated by Eq. (10).

3. Calorimeter

Calorimeter based on the principle described is designed so as to measure isobaric specific heat capacity for fluids and fluid mixtures at high temperatures and high pressures. New calorimeter assembled in a pressure vessel is shown in Fig. 2. The calorimeter in cylindrical shape is surrounded by nitrogen gas which works as a poor conductor of heat. Pressure of the nitrogen gas is measured and controlled by dead weight pressure gauge. A metal-bellows made of inconel 718 is welded with the cylindrical part of the calorimeter which is made of SUS 316 and 2.5 mm in thickness. Sample container (78.5 mm long, 40 mm in outer diameter) consists of these two parts and its thickness is designed as thin as possible. A heater (2 W and 1.6 mm in diameter) is installed in the lowest part of the calorimeter. It is also equipped with five platinum resistance thermometers for measuring temperature and temperature distribution of the sample. Position of five platinum resistance thermometers is shown in Table 1. At the other side of the calorimeter a displacement sensor is attached for detecting position of the side of the calorimeter. The pressure vessel is designed for pressures up to 20 MPa and is immersed in a thermostatted oil bath as shown in Fig. 3. The bath works in a temperature range from 250 K to 500 K. Figure 4 shows measurement system of temperature and pressure as well as the assembly of valves and tubings.

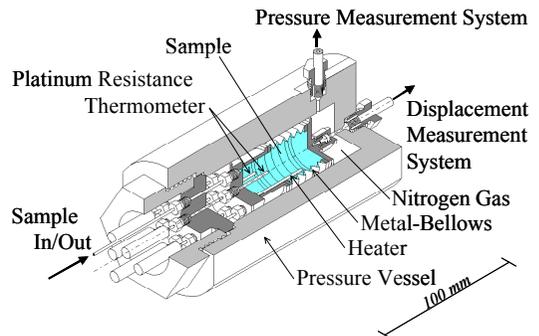
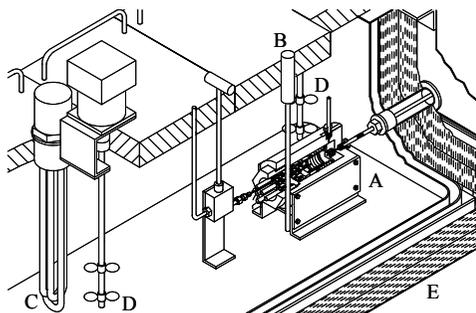


Fig. 2. Drawing of calorimeter.

Table 1. Position of platinum resistance thermometers (PRT)

	PRT1	PRT2	PRT3	PRT4	PRT5
length [mm] from side	40	10	10	25	40
position	upper left	lower left	upper right	center	lower right



A: Calorimeter, B: Platinum resistance thermometer, C: Heater, D: Stirrer, E: Thermostatted oil bath

Fig. 3. Configuration of calorimeter in the oil bath.

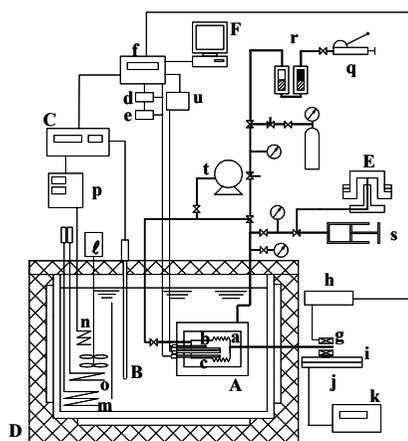
A: Pressure vessel, B: Platinum resistance thermometer, C: Thermometer bridge, D: Thermostatted oil bath, E: Air-piston pressure gauge, F: Personal computer, a: sample container, b: Platinum resistance thermometer, c: heater, d: Standard resistance, e: Regulated DC power supply, f: Digital multi-meter, g: Liner variable differential transformer, h: Displacement meter, i: Liner stage, j: Liner gauge, k: Indicator, ℓ : Stirrer, m: Main heater, n: Supplemental heater, o: Cooler, p: PID-controller, q: High pressure pump, r: Intensifier, s: Pressure controller, t: Vacuum pump, u: Resistance measurement circuit

Fig. 4. Measurement system.

4. Procedure

After the sample of known mass is loaded into the calorimeter, temperature of the bath and pressure of the nitrogen gas in the pressure vessel are controlled constant. Equilibrium condition of the sample in the calorimeter is confirmed and the position of the calorimeter is measured by displacement system. Then, heat flow at constant rate is supplied to the sample by the heater in the calorimeter. Increasing temperature of the sample is measured by five thermometers at an interval of 2 s until the temperature becomes constant. If these data can be fitted well to Eq. (7) with constant relaxation time, the isobaric specific heat capacity for the sample can be calculated by Eq. (11).

$$c = (\alpha\tau - C_a)/m \quad (11)$$

5. Discussion on lumped system analysis

Figure 5 shows temperature difference for water measured by five different thermometers as a function of time at 0.1 MPa and 323.15 K with a heating power of 0.882 W. The temperature difference from the average value was within ± 0.1 K during the heating process for $\Delta T_{\max} = 5.741$ K. Figure 6 shows that the relaxation time was kept constant during the heating process. In the light of the results shown in Figs. 5 and 6, new calorimeter satisfies practically the criteria for lumped system.

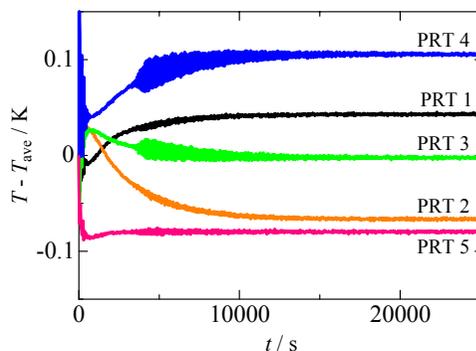


Fig. 5. Temperature distribution of water at 323.15 K and 0.1 MPa with a heating power of 0.882 W.

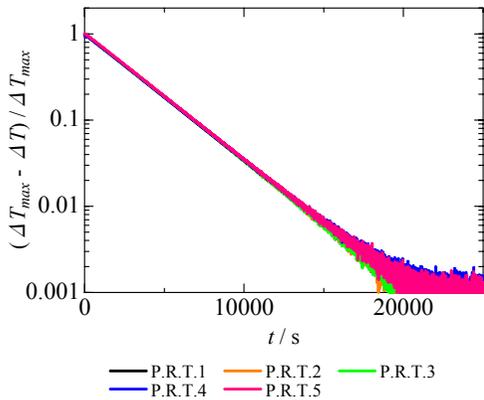


Fig. 6. Heating curves of water at 323.15 K and 0.1 MPa with a heating power of 0.882 W.

6. Calibration

Thermal conductance α given in Eq. (8) varies with heat transfer coefficient h for heat flow from the calorimeter and its surface area A . h depends on the temperature difference ΔT_{\max} and conditions P and T of nitrogen gas outside the calorimeter. A can be calculated by measurements of the displacement L of the calorimeter. Thus, α can be expressed by

$$\alpha = \alpha(P, T, \Delta T_{\max}, L). \quad (12)$$

For calibration of α and C_a , we conducted three series of measurements at 323.15 K and 0.1 MPa with different surface areas of the calorimeter and different heat supply. Two series have been carried out with water, and one series with toluene as shown in Table 2. The results are shown in Fig. 7. Using c_p value of the IAPWS[1] for water and that of Scott et al.[2] for toluene as reference values, we determined α and C_a as

$$\alpha = \alpha_0 + \alpha_1 \Delta T_{\max} + kL, \quad (13)$$

$$C_a = 149.9 \text{ J/K}. \quad (14)$$

Table 2. Heat capacity values measured.

	m [g]	L [mm]	c_p [kJ/(kg·K)]	mc_p [J/K]
water ser.1	41.915	-0.898	4.180	175.2
water ser.2	40.065	0.793	4.180	167.5
toluene	34.593	0.127	1.785	61.7

7. Results

Methanol of 32.274 g has been loaded to the calorimeter and its c_p value has been measured at 323.15 K and 0.1 MPa. The result is shown in Fig. 8 with literature values on c_p - T plane. Comparison of the result with literature data confirms reliability of new calorimeter.

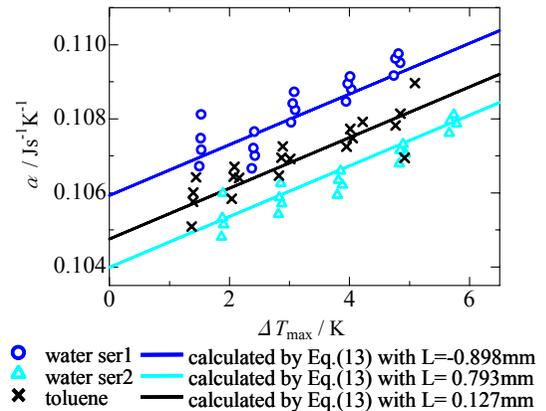


Fig. 7. Results of thermal conductance as a function of ΔT_{\max} at 323.15 K and 0.1 MPa.

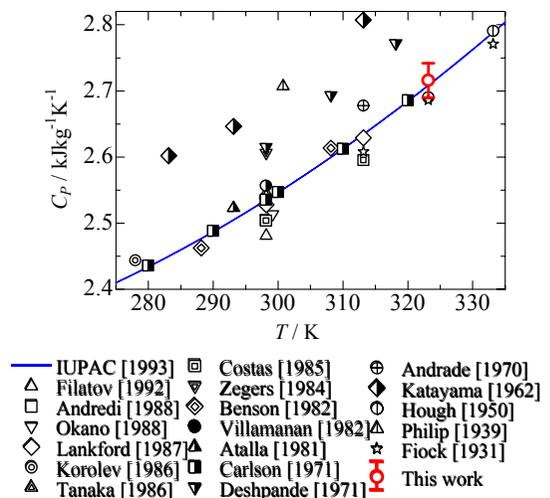


Fig. 8. Result at 323.15 K and 0.1 MPa and comparison with literature values.

References

- [1] W. Wagner and A. Pruß : *J. Phys. Chem. Ref. Data*, **31**(2), 387(2002).
- [2] D.W. Scott et al. : *J. Phys. Chem.*, **66**, 911(1962).