

A New Apparatus for the Measurement of the Isobaric Heat Capacity of Liquid Refrigerants¹

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A new automated adiabatic flow calorimeter was developed which enables one to measure the isobaric heat capacity, C_p , of pure fluids and their mixtures in the liquid phase. The calorimeter has been carefully designed to keep the heat loss from the sample fluid as small as possible being regarded as negligible. The experimental apparatus constitutes a closed circuit of the sample circulation using a combination of two mounted metallic bellows and a metering pump. The present apparatus is designed to measure C_p at temperatures to 500 K and pressures to 15 MPa and is also applicable to measurements in the critical region as well as the region near the saturated liquid state because of its excellent mass flow rate control stability and the high adiabatic efficiency of the calorimeter. The C_p of liquid refrigerant 114 (R114) has been measured at temperatures from 275 to 415 K and pressures up to 3.2 MPa including the critical region with experimental uncertainty of less than $\pm 0.4\%$. The heat capacity of saturated liquid R114 has also been derived from the data measured in the single phase.

KEY WORDS: dichlorotetrafluoroethane; flow calorimetry; isobaric heat capacity; liquid; R114; refrigerants; saturated liquid.

1. INTRODUCTION

The values of isobaric heat capacity, C_p , of refrigerants, especially in the liquid phase often exhibit considerable differences between the existing tabulated values and the derived values from available equations of state. For example, in the case of R114 (dichlorotetrafluoroethane), whose thermophysical properties are better known than those of other refrigerants,

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there exist large differences as shown in Fig. 6. The major reason might be the scarcity of data due to the experimental difficulty of obtaining C_p in the liquid phase. Presently, no experimental C_p data are available for refrigerant mixtures.

Based upon the above viewpoint, a novel apparatus for measuring C_p of pure fluids and their mixtures on an absolute basis has been designed and constructed so as to cover the range of temperatures to 500 K and of pressures to 15 MPa. The principle of the measurement is based upon flow and adiabatic calorimetry. An automated mass flow meter was developed enabling experimental data to be obtained almost automatically. The reliability of the apparatus has been confirmed for C_p measurements of water and R114 as discussed below.

The C_p of R114 in the liquid phase and in the critical region was measured with an uncertainty of less than $\pm 0.4\%$. We derived the C_p at saturated liquid states, C'_p , and then develop a C'_p correlation for R114.

2. PRINCIPLE

Flow calorimetry has been used mainly for measuring the C_p at gaseous phases in previous investigations. This method requires that the temperature of a flowing sample fluid be kept uniform by developing turbulent flow for the gas. On the other hand, however, it is difficult to apply this method to the liquid, because it requires high mass flow rates, which result in unsteady liquid flow or inaccurately measuring the mass flow rate. Hence, we have tried to keep the temperature uniform in the sample liquid via an extremely low flow rate. This means that precise flow control together with complete adiabatic performance of the calorimeter becomes essential for C_p measurements in the liquid phase.

The principles of measurement have been discussed in our previous paper [1]. The previous apparatus had a different circulation system but the same calorimeter as in the present study. Flow calorimetry consists of three simultaneous measurements, i.e., constant heat flux, \dot{Q} , temperature increment, ΔT , defined as the difference between the temperature of the sample fluid before and that after heating, and constant mass flow rate, \dot{m} .

The C_p is defined by the following relation:

$$C_p = \dot{Q}/(\Delta T\dot{m}) \quad (1)$$

Heat loss from the sample fluid is always unavoidable in calorimetry so that Eq. (1) should be modified so as to take into account the heat loss as

$$\begin{aligned}
 C_{\text{pexp}} &= (\dot{Q} - \dot{Q}_L)/(\Delta T \dot{m}) \\
 &= \dot{Q}/(\Delta T \dot{m}) - \dot{Q}_L/(\Delta T \dot{m}) \\
 &= C_p - \dot{Q}_L/(\Delta T \dot{m})
 \end{aligned}
 \tag{2}$$

where \dot{Q}_L denotes the heat loss from the sample fluid, and C_{pexp} is the observed C_p value obtained by the calorimeter.

If \dot{Q}_L is independent of mass flow rate, the effect of heat loss to the C_{pexp} will become small with increasing mass flow rate as shown by Eq. (2) so that the intrinsic C_p value may be defined at infinite mass flow rate (inverse mass flow rate is zero at this point).

When the heat loss is large, however, this method may lose reliability for C_p measurements because of its extrapolation technique for determining the intrinsic C_p values at infinite mass flow rate. Therefore, we have attempted to minimize the heat loss as much as possible allowing C_{pexp} to be independent of mass flow rate. Thus, the principle of the present calorimetry can be called adiabatic flow calorimetry.

3. APPARATUS

The characteristic features of this apparatus are the adiabatic performance of the calorimeter, closed circulation system, and stable sample liquid flow. The automated mass flow meter developed in this study is always connected to the circulating system by fine-bore tubings, so the mass flow rate may be measured continuously and automatically.

The calorimeter used in this study is shown in Fig. 1. A detailed description has also been given in our previous paper [1]. The calorimeter has been installed in the thermostated bath and the sample temperature is allowed to reach thermal equilibrium with the bath temperature after passing through the preheating zone. The calorimeter consists of the 100- Ω inlet and outlet platinum resistance thermometers and a microheater. The thermometers and microheater have been inserted into 1.6-mm-outer diameter stainless-steel tubes. The 1.6-mm-outer diameter tube in which the microheater is installed is inserted in the 6.35-mm-outer diameter stainless-steel tube which is used as the inner shield in Fig. 1.

The sample liquid flows from the inlet as shown in Fig. 1, where its temperature is measured by the inlet thermometer. Then the sample flows through the tubing inside the calorimeter and receives an electrically induced heat flux from the microheater. The direction of the liquid flow is designed to follow natural convection, minimizing convective heat loss. After heating the sample liquid temperature is measured by the outlet thermometer.

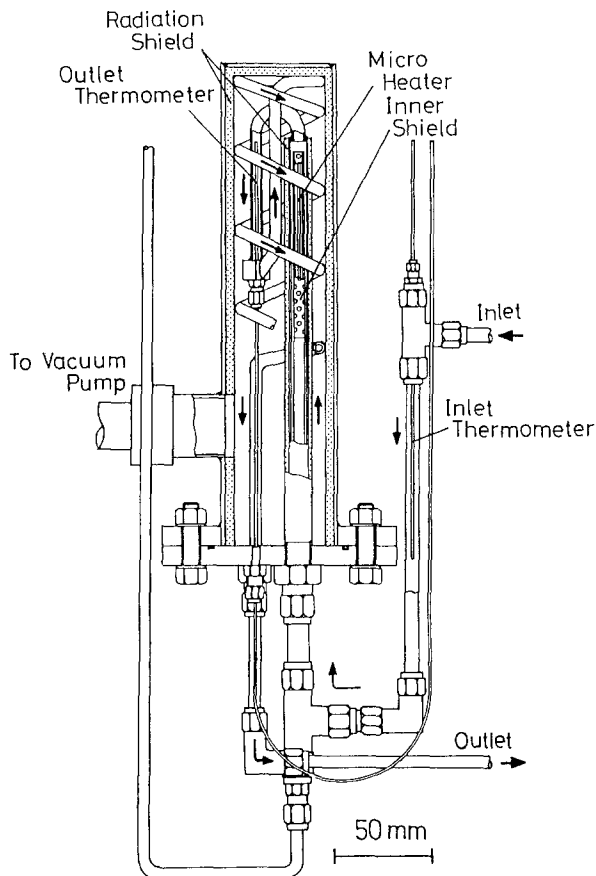


Fig. 1. Flow calorimeter.

The sample liquid does not flow out directly to the outside of the calorimeter but flows through the long spiral tubes in order to avoid not only convective heat loss from the tubing but also radiative heat loss from the sample liquid by keeping the temperature inside the calorimeter the same as the temperature of the heated sample liquid.

The inner surface of the calorimeter is covered with the multilayered aluminum foil radiation shield shown in Fig. 1. Also, the inside of the calorimeter is kept at a high vacuum, eliminating radiative heat loss as well as conductive heat loss by the remaining gases.

A schematic diagram of the recirculating constant-flow assembly is shown in Fig. 2. The flow assembly is filled with sample completely in the liquid phase.

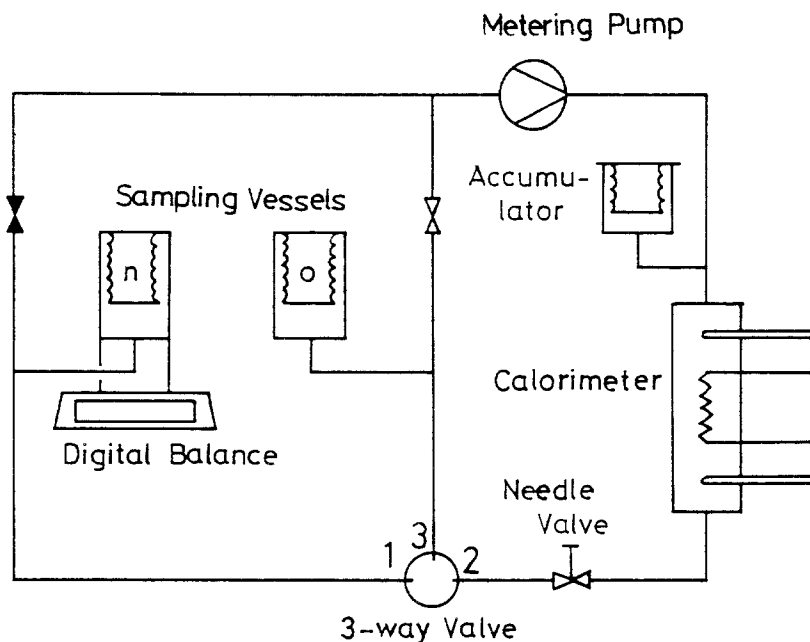


Fig. 2. Schematic diagram of constant-flow assembly.

The sample liquid circulates certainly at a constant flow rate between two pressure levels in the system, the higher-pressure level at the accumulator and the lower pressure level at the sampling vessels. The two different pressures at the accumulator and sampling vessels are kept at required pressure levels by means of nitrogen gas filled in metallic bellows. The thermodynamic condition of the system can be monitored by the difference between the inlet and the outlet temperatures at a constant heat flux from the microheater. After achieving thermodynamic equilibrium in the system, the three-way magnetic valve is switched to connect the sampling vessel (n) with the calorimeter via numbers 1 and 2, respectively, in Fig. 2. Then the sample liquid flows from the sampling vessel (o) to another sampling vessel (n) through the metering pump, accumulator, calorimeter, and needle valve. The sample fluid is then collected in the sampling vessel (n) during a certain time period. Then the mass increase in the sampling vessel (n) is automatically measured by a digital mass balance. The further detailed experimental assembly is shown in Fig. 3.

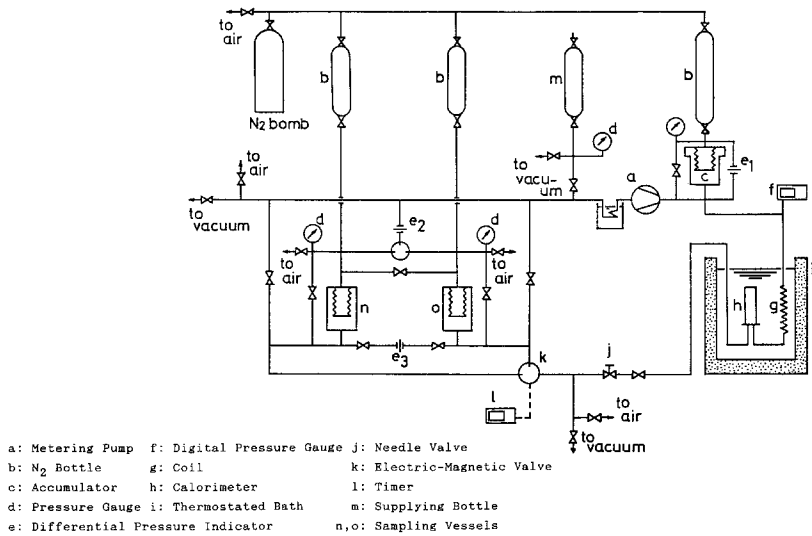


Fig. 3. Experimental assembly.

4. EXPERIMENTAL ERRORS AND CALIBRATION

The uncertainty of the respective instruments used for measuring C_p in the present study is summarized in Table I. The inlet and outlet thermometers have been calibrated using a standard 25- Ω platinum resistance thermometer which was calibrated at the National Research Laboratory of Metrology, Ibaraki, Japan, according to IPTS-68. The uncertainty of the

Table I. The Uncertainties of the Measurements

Parameter	Device	Uncertainty
ΔT	Platinum resistance thermometer	± 5 mK
\dot{m}	Digital balance	$\pm 0.04\%$
	Times	$\pm 0.006\%$
\dot{Q}	Digital multimeter	$\pm 0.02\%$
P	Bourdon-type digital pressure gauge	2.9 kPa
T	Inlet thermometer and thermostated bath	± 10 mK
Total uncertainty of measured C_p due to random errors		$\pm 0.4\%$

temperature increment is estimated to be less than ± 5 mK, whereas the thermostated bath temperature is regulated within ± 10 mK.

The pressure is measured directly by a Bourdon-type digital pressure gauge with a sensitivity of 0.1 kPa. This pressure gauge has been calibrated with a precise deadweight pressure gauge and the uncertainty of the measured pressure is estimated to be less than ± 2.9 kPa even when taking the maximum deviation of calibration into consideration.

The heat flux is generated by a DC electric microheater. Voltage and current measurements are obtained using a digital multimeter with the aid of a $1\text{-}\Omega$ standard resistor, and hence the uncertainty of the measured heat flux is estimated to be less than $\pm 0.02\%$.

In mass flow measurements, since the uncertainty of the digital balance is ± 5 mg and the mass increase is between 12 and 15 g, the systematic errors of the sample mass measurement are less than $\pm 0.04\%$. The uncertainty of time measurement using a quartz timer is less than $\pm 0.006\%$.

The effect of the connecting tubing of the sampling vessel (n) must be considered very carefully as a major part of the systematic errors in the mass measurement. The following tests have been performed regarding the examination of this effect:

- (1) test by using the balance weights;
- (2) comparison with the previous C_p data which were measured by the previous apparatus (In the previous procedure, the mass measurements were performed by the digital balance after disconnecting the sampling vessel from the line);
- (3) reproducibility test under the condition of a constant mass increase during different sampling time periods; and
- (4) reproducibility test under the condition of different mass increases during the same sampling time period.

From preliminary tests mentioned above, we obtained the following results:

- (1) agreement was within ± 5 mg, which is equal to the uncertainty of balance;
- (2) there was no systematic change between the present results and previous data measured by Sato et al. [1] with an accuracy of less than $\pm 1\%$ as shown in Fig. 4;
- (3) no effect of sampling time difference has been observed; and
- (4) no effect of mass difference variation has been observed.

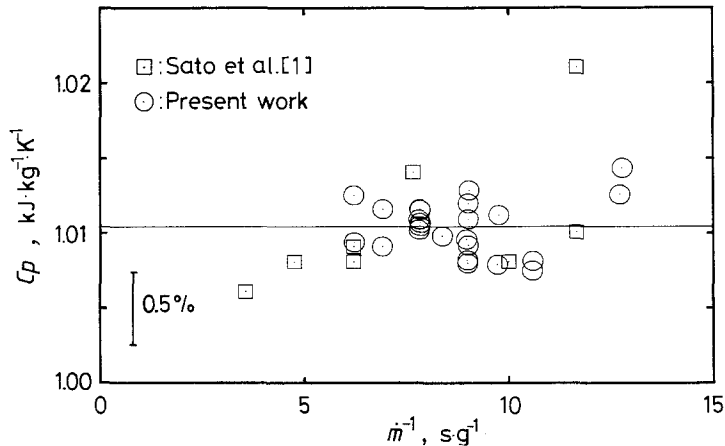


Fig. 4. Reproducibility in C_p measurements for liquid R114 at 310 K and 0.5 MPa at various inverse mass flow rates.

No systematic error due to the effect of connecting tubing was observed in the tests.

Many C_p values of liquid R114 at 310 K and 0.5 MPa have been measured at various mass flow rates as shown in Fig. 4. Note that the heat loss from the calorimeter generally appears as a slope of the regression line as discussed in Section 2. In the case of the present experimental data, however, such a slope is not apparent. In other words, the present experimental C_p values do not depend on the mass flow rate. Therefore, it has been concluded that the heat loss from the calorimeter is so small as to be negligible, as expected.

In addition, these results have been compared with the previous data in Fig. 4 which have been reported under the same conditions by Sato et al. [1]. Sato et al. measured the C_p at various mass flow rates by using the same calorimeter but a different flow system and confirmed its reliability by measuring the C_p values of water. The systematic errors were not found and the standard deviation from the equation of state developed by Sato et al. [3] was 0.34%. Figure 4 shows no systematic errors among the data for R114 and random errors smaller than those of the previous data.

The uncertainty of the measured C_p value has been concluded to be less than $\pm 0.4\%$, according to the amount of random error.

5. MEASUREMENTS FOR DICHLOROTETRAFLUOROETHANE (R114)

The present experimental results for R114 are shown in Fig. 5. The current 31 data points and 24 data points reported in our previous paper

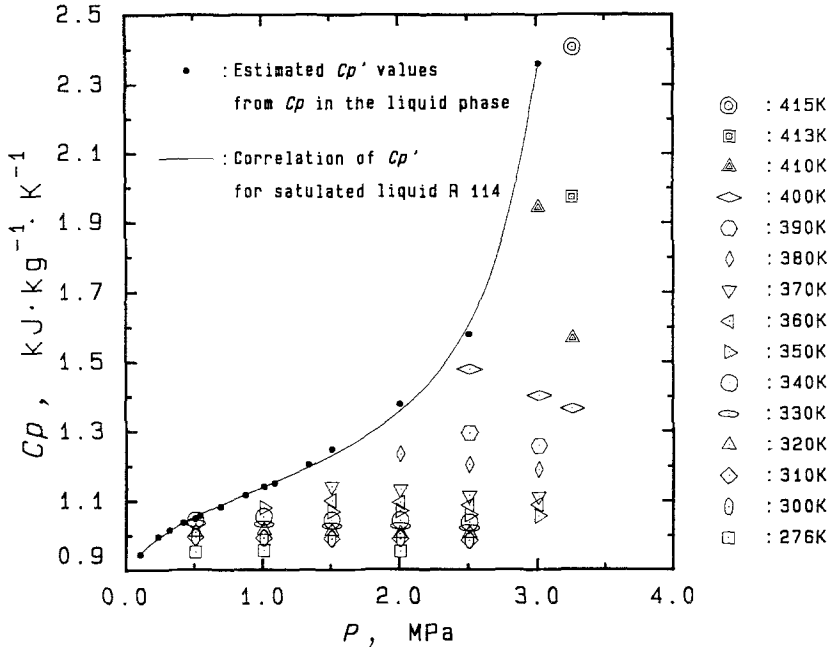


Fig. 5. Experimental data and the correlation of C_p' for saturated liquid R114.

[1, 2] are shown at pressures between 0.5 and 3.2 MPa and at temperatures between 276 and 415 K. The C_p values in this study have been measured along isobars or isotherms. And the C_p' for the saturated liquid R114 was determined by applying an extrapolation technique along each isobar and isotherm fitting simple polynomials by least squares. The vapor pressure was determined on the basis of the equation developed by Ashizawa et al. [8].

The heat capacity value plotted in Fig. 5 has been determined from three to five observations of the same state parameters at different mass flow rates. The temperature increment, ΔT , was fixed as 5 K for all measurements to keep a high reliability, while in the case of measurements near the saturation curve or at higher temperatures, above 390 K, measurements with ΔT of 3 and 1 K were also performed in order to confirm the difference between the measurements with ΔT of either 3 or 1 K and those with ΔT of 5 K being smaller than the experimental error. The C_p increases with increasing temperatures, and the behavior of the C_p follows the general trend, being infinite at the critical point (418.78 K, 3.252 MPa [9]) as expected.

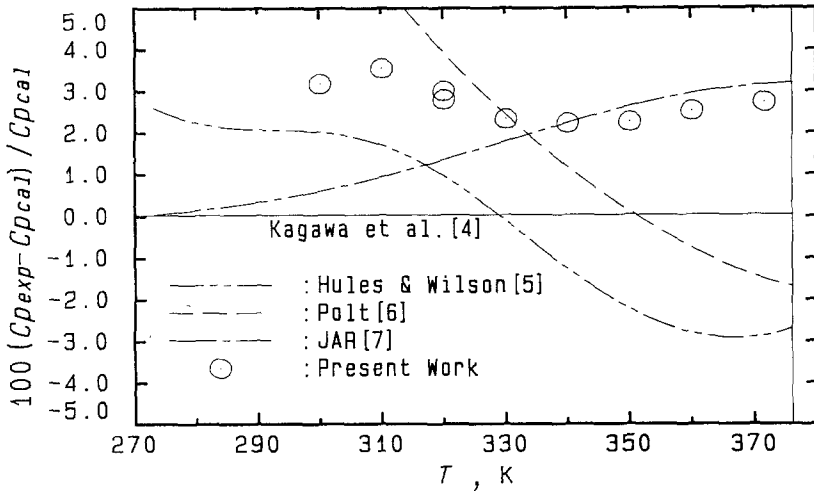


Fig. 6. Deviation plots from the equation of state developed by Kagawa et al. [4] regarding C_p measurements of R114 in the liquid phase along the 2.5-MPa isobar.

These C'_p values for the saturated liquid R114 were correlated with the expression,

$$C'_p = \exp[-3.99846 \times 10^{-3}(1 - T_r)^{-1.3} + 3.91408 \times 10^{-2}(1 - T_r)^{-0.9} - 9.99133 \times 10^{-1}(1 - T_r)^{1.7} + 9.63991 \times 10^{-1}(1 - T_r)^{3.7}] \quad (3)$$

where $T_r = T/T_c$ and C'_p is given in $\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ and T in K. This correlation is effective in the range of temperatures between 276 and 414 K.

As an example, a comparison of the present results with available equations of state in the liquid phase at 2.5 MPa is shown in Fig. 6. Kagawa et al. [4], Hules and Wilson [5], Polt [6], and the Japanese Association of Refrigeration (JAR) [7] have reported equations of state for R114. The values of the JAR agree with the present results at higher temperatures, above 340 K, along the 2.5-MPa isobar, but other equations differ from the present results considerably.

The purity of the sample R114 is 99.97 wt%, being an isomeric blend of 95% dichlorotetrafluoroethane ($\text{CClF}_2\text{CClF}_2$) + 5% 1,1-dichloro-1,2,2,2-tetrafluoroethane (CCl_2FCF_3).

The uncertainty of C_p measurements is estimated to be less than $\pm 0.4\%$ and uncertainties of the state parameters are ± 10 mK for temperature and ± 2.9 kPa for pressure, respectively.

6. CONCLUSION

The adiabatic flow calorimeter for measuring the C_p in the liquid phase was developed and constructed. The heat loss from the sample fluid has been confirmed as being negligibly small. The stability of sample liquid flow and the reliability of the automated mass flow meter have also been confirmed.

Precise C_p measurements for R114 in the liquid phase have been carried out at temperatures from 276 to 415 K and pressures from 0.5 to 3.2 MPa with the estimated maximum uncertainty of $\pm 0.4\%$. The results compared with available equations of state exhibit differences between the derived values from equations and the present results. The C_p' values for saturated liquid R114 have been determined from the C_p data in the single phase.

The C_p data for many pure substances and their mixtures will be obtained over a wide range of state parameters including the liquid and the supercritical region with a better accuracy in the future.

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