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J. of Supercritical Fluids 46 (2008) 258–264

THE JOURNAL OF Supercritical Fluids

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High-pressure isobaric heat capacities using a new flow calorimeter

José J. Segovia*, David Vega-Maza, César R. Chamorro, M. Carmen Martín

Research Group TERMOCAL-Thermodynamics and Calibration, University of Valladolid, Paseo del Cauce s/n 47011, Valladolid, Spain

Received 30 July 2007; received in revised form 14 January 2008; accepted 18 January 2008

Abstract

An automated flow calorimeter has been developed for the measurement of high accurate isobaric heat capacities for pure compounds and mixtures over the range 250–400 K and 0–20 MPa. The technique has been checked for different compounds and at different conditions of temperature and pressure and the results have been compared with the literature values available. The conclusion of this comparison is that the new calorimeter can measure heat capacities with an estimated total uncertainty better than 0.5%. This paper report describes the new equipment, its set-up and gives new heat capacity data for toluene and ethyl *tert*-butyl ether at different temperatures and pressures.

Keywords: Isobaric heat capacity; High pressure; Toluene; ETBE; Flow calorimeter

1. Introduction

Heat capacities are basic thermophysical properties of a fluid. Data on heat capacities as a function of temperature are required for energy balances in chemical or energy processes and for the design and control stages. Variations in heat capacities are also useful for understanding changes in the structure of fluids, even isobaric heat capacity data at different pressures can be used to validate equations of state [1].

The equation of state and heat capacity are the basic thermodynamic data which allow other useful properties, such as changes in enthalpy, Gibbs energy or entropy, to be calculated using only the thermodynamic relationships. The knowledge of *pvT* data and heat capacities over a wide range of temperatures and pressures for a mixture allows a complete thermodynamic characterization of the mixture to be obtained.

There are many interesting mixtures from an industrial point of view, but our group has focused the research on the characterization of new environmentally friendly fuels such as natural gas, reformulated gasolines or bio-fuels. The transport sector accounts for more than 30% of final energy consumption in the European Community and is expanding, a trend which is bound to increase, along with carbon dioxide emissions and another pollutants. In this context, the study of alternative fuels is very important.

The group has experience in different experimental techniques and the laboratory is well equipped with them. One of their main characteristics is the high accuracy of the measurements obtained. In order to complete the thermodynamic data of liquids, we have developed a calorimeter for measuring heat capacities over a wide range of temperatures and pressures [2].

2. Theoretical part

Before giving a detailed description of the new calorimeter, it is useful to point out the main thermodynamics relationships related to heat capacities.

The temperature derivative of the internal energy at constant volume gives the heat capacity at constant volume:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,x_i} \quad (1)$$

The temperature derivative of the enthalpy at constant pressure gives the heat capacity at constant pressure which is also related to the second temperature derivative of the Gibbs energy:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_{p,x_i} = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,x_i} \quad (2)$$

The difference between them is given as

$$C_p - C_V = \frac{TV\alpha_p^2}{\kappa_T} \quad (3)$$

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[*] Corresponding author. Tel.: +34 983 184690; fax: +34 983 184690.
E-mail address: josseg@eis.uva.es (J.J. Segovia).

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doi:10.1016/j.supflu.2008.01.011

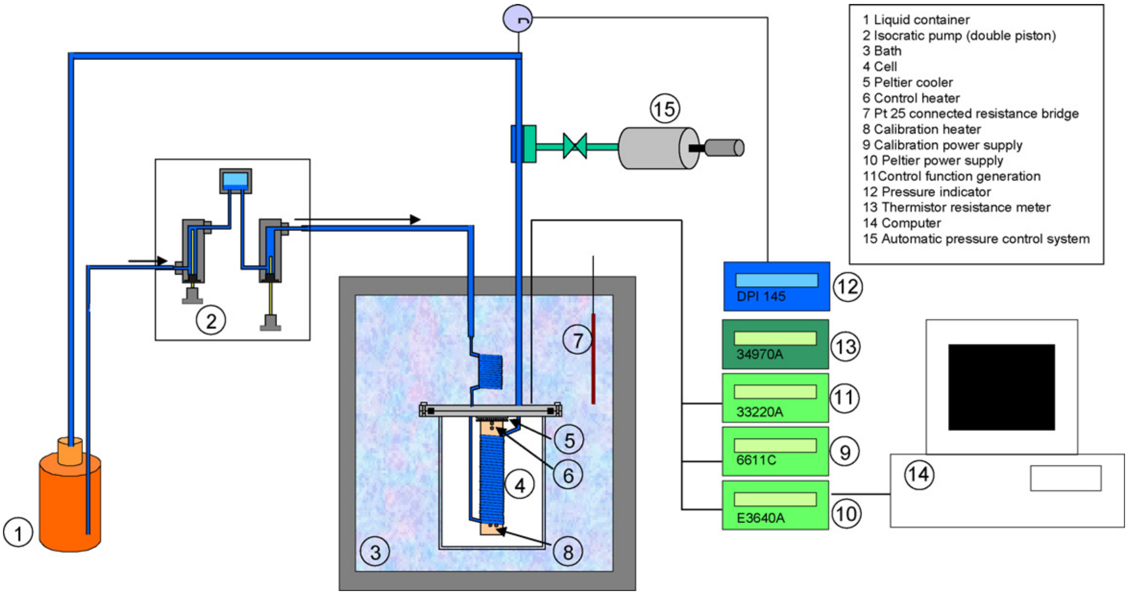

Fig. 1. A schematic view of the new calorimetric technique.

where α_p is the isobaric expansivity and κ_T is the isothermal compressibility.

The heat capacity dependence on pressure or volume is determined through pvT data:

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p = -T\left(\alpha_p^2 + \left(\frac{\partial \alpha_p}{\partial T}\right)_p\right) \qquad (4)$$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = -T\left(\frac{\partial^2 p}{\partial T^2}\right)_V \qquad (5)$$

and its dependence on temperature is experimentally obtained by calorimetry.

According to the enthalpy equation, for non-isobaric processes, the enthalpy change can be obtained through Eq. (6):

$$\mathrm{d}h = C_p\,\mathrm{d}T + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right]\mathrm{d}p \qquad (6)$$

Most of the techniques operate at constant pressure, and can be measured by putting the sample in a container (static method) or circulating it in the calorimetric cell (dynamic method).

3. Method description

The calorimeter we have designed is a flow calorimeter. The main advantages of this type of technique are no vapour space, great sensitivity, rapid results and good accuracy.

It is based on the simultaneous heating and cooling of the calorimetric cell to maintain a fixed difference between the inlet and exit temperatures of the circulating fluid at constant flow rate. Heat capacity is calculated by the determination of the net power exchanged.

A schematic view of the calorimeter is shown in Fig. 1. A precision isocratic pump with dual floating pistons in series (Agilent 1100 used in HPLC chromatography) delivers the liquid through the cell at a programmable constant flow rate. The fluid passes through a loop immersed in the bath to ensure that it reaches the bath temperature prior to entering the cell. The cell is a stainless steel vessel containing a copper block where all the energy in the process is exchanged by conduction. The liquid flows through a stainless steel tube which is coiled around the copper block. A detailed view of the measuring cell is shown in Fig. 2. The fluid decreases in temperature as it moves along the cell because the calorimeter works with a constant difference between the inlet and outlet temperatures of 0.5 K. To achieve this condition, a Peltier cooler removes energy at a constant rate from the cell and a control-heater compensates for this energy loss to maintain the desired temperature difference. The fluid exit temperature is measured by an NTC thermistor and the inlet temperature using a calibrated standard Pt-25 thermometer with an a/c resistance bridge ASL700 as an indicator. The fluid inlet temperature is also the bath temperature in which the cell is immersed. The Peltier cooler, the control-heater and the calibration heater are each con-

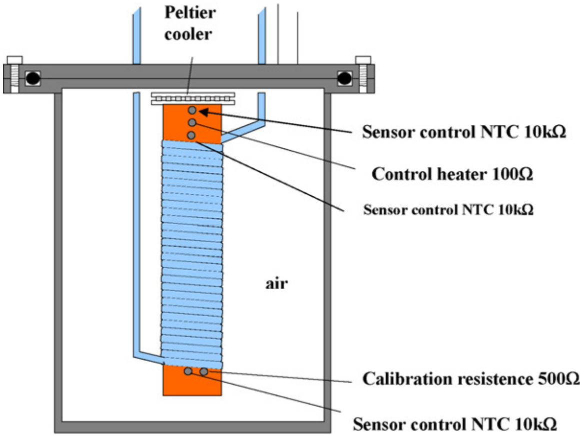

Fig. 2. A detailed view of the flow cell of the calorimeter.