



Investigation of the melting behavior of the reference materials biphenyl and phenyl salicylate by a new type adiabatic scanning calorimeter



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ARTICLE INFO

Article history:

Received 6 October 2013

Received in revised form 15 February 2014

Accepted 22 February 2014

Available online 3 March 2014

Keywords:

Adiabatic scanning calorimetry

Enthalpy

Heat capacity

Melting transition

Biphenyl

Phenyl salicylate

ABSTRACT

Simultaneously measured high-resolution enthalpy and heat capacity data are obtained by means of a novel type Peltier-element-based adiabatic scanning calorimeter that can also operate as a classical adiabatic heat-step calorimeter. Specific enthalpy and specific heat capacity results with 2% uncertainty and sub-mK temperature resolution are presented for the melting transition of the calorimetric reference materials biphenyl and phenyl salicylate. The simultaneously obtained enthalpy and heat capacity data allow for a simplified and reliable purity analysis.

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1. Introduction

Many fields of research and applications require detailed information on thermal properties of condensed matter systems. In particular, the temperature dependence of the energy or enthalpy $H(T)$ of a sample of a given substance is important. Although, as we will see further, the direct measurement of $H(T)$ is possible, in many cases one only has direct experimental access to the heat capacity $C_p = (\partial H / \partial T)_p$, the slope of the enthalpy curve as a function of temperature. The enthalpy curve itself requires then an additional integration. This approach cannot work properly when there is a discontinuity in the enthalpy curve (latent heat) at a first-order phase transition, where the essential information on the latent heat cannot be obtained from C_p data alone and a direct measurement (in steps or by scanning) of the enthalpy is necessary.

Several types of calorimetric methodologies have been developed in the past with different degrees of uncertainty and resolution depending on the application envisioned. For low-uncertainty data, one usually employs a classical adiabatic (heat-step) calorimeter [1–4]. After the commercial introduction

in the 1960s of differential scanning calorimeters (DSC), the use of these types of instruments has become widespread in thermal analysis [5–8]. Other heat capacity measuring techniques have been developed, such as ac-calorimetry [9,10], the 3ω method [11], and photoacoustic and photopyroelectric techniques [12,13].

Another technique, adiabatic scanning calorimetry (ASC) has only received limited attention so far. It was introduced in the late 1970s by a group at KU Leuven (Belgium) for high-resolution measurements of the heat capacity and enthalpy near phase transitions and critical points in liquid mixtures and liquid crystals [14,15]. The innovation introduced was to apply under adiabatic conditions a constant, known electrical power to the sample cell instead of imposing a constant rate (as done in DSC-type calorimeters). With the power and temperature evolution known, the heat capacity and enthalpy of the sample can be calculated with high resolution [16]. However, ASCs remained largely research instruments not the least because of complicated sample cell mounting and elaborate construction to impose adiabatic conditions. These problems have been eliminated in a new design of ASCs by incorporating Peltier elements between the sample cell and the adiabatic shield [17,18]. Measurements, over large temperature ranges on mg-sized samples, are now possible with high resolution in temperature (sub-mK), enthalpy and heat capacity. Accurate data can be obtained by a one-time calibration of the incorporated thermometers and of the background heat capacity of the sample cell and addenda.

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In this work, we illustrate the possibilities of the novel Peltier-element-based adiabatic scanning calorimeter (pASC) by a series of measurements on biphenyl and phenyl salicylate (salol) near their melting point. In a first part, the ASC concept and the novel implementation will be discussed. Subsequently, high-resolution enthalpy and heat capacity data will be presented and discussed for both compounds. Attention will also be paid to impurity determination. Biphenyl and phenyl salicylate were chosen because high-purity samples of these compounds are being used as calibration substances for DSC instruments [19]. The DSC technique is a dynamic technique and the quality of DSC measurements is influenced by parameters related to the instrument, the scanning rate, the sample and the operator, and depends critically on the quality of the frequent temperature and caloric calibration of the instrument [19–21]. For the calibration of a DSC, one is strongly dependent on high-purity reference materials accurately characterized by absolute calorimetric techniques as adiabatic heat-step calorimetry [22–25].

2. Experimental

2.1. Methodology of adiabatic scanning calorimetry

Adiabatic scanning calorimetry (ASC) is a calorimetric technique aimed at the simultaneous measurement of the temperature dependence of the enthalpy and the heat capacity of condensed matter materials. The basic concept of ASC resides in applying a constant heating or cooling power to a sample holder containing a sample. This is opposite to what is done in DSC where a constant heating rate is imposed and the changing power needed to maintain the constant rate is measured in a differential approach with a reference sample. In ASC the sample holder is placed in a surrounding adiabatic shield allowing to cancel (heating mode) or to control (cooling mode) continuously the heat exchange between the sample holder and the shield during scanning with a known constant heating or cooling power applied to the sample holder. During a run the sample temperature $T(t)$ is recorded as a function of time t , and the heat capacity $C(T)$ as a function of temperature is calculated via the ratio of the known constant power P and the changing temperature rate $\dot{T} = dT/dt$:

$$C(T) = \frac{P}{\dot{T}}. \quad (1)$$

This leads to a continuous heat capacity curve. Moreover, the same $T(t)$ data and the known power P directly result in the enthalpy curve, since

$$H(T) - H(T_0) = \int_{t_0}^{t(T)} P dt = P(t - t_0), \quad (2)$$

where $H(T_0)$ is the enthalpy of the system at the start time t_0 of the experiment. It is a direct consequence of the constant power requirement that the integral can be simply solved. The ASC measurement methodology is schematized in Fig. 1 for a weakly first-order transition with substantial pre-transitional enthalpy and heat capacity variation below and above a small latent heat discontinuity in the enthalpy at T_{trans} . Although schematic, the depicted heat capacity and enthalpy temperature dependencies are representative for many weakly first-order phase transitions, as for example the nematic–isotropic transition (clearing point) in liquid crystals [26,27].

2.2. Peltier-element-based adiabatic scanning calorimeter (pASC)

An essential requirement of a high-resolution adiabatic scanning calorimeter operating in a (slow) heating mode is the equality

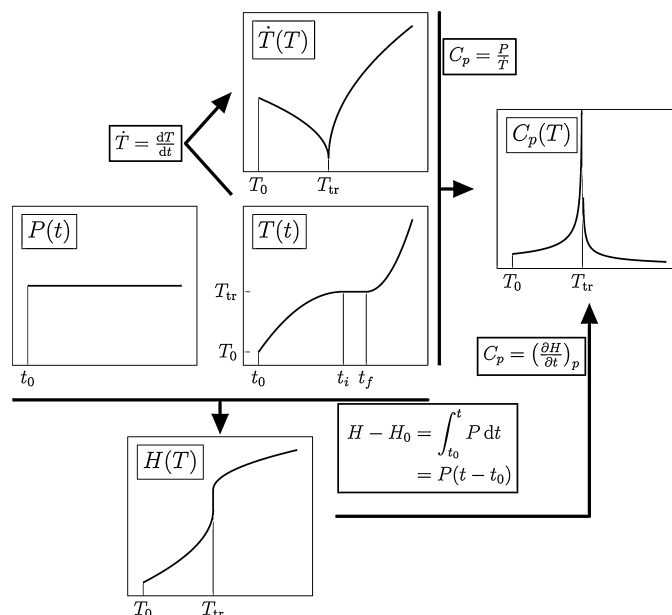


Fig. 1. Schematic representation of the treatment of the directly measured $T(t)$ and $P(t)$ data in a constant power heating run for a weakly first-order transition, with anomalous pre-transitional enthalpy and heat capacity changes, to arrive at results for the heat capacity (at constant pressure) $C_p(T)$ and enthalpy $H(T)$. T_0 is the starting temperature of the run at the time t_0 . t_i and t_f are the beginning and the end of a first-order transition at T_{trans} .

(mK or better) of the temperatures of the adiabatic shield and the sample (holder) in weak thermal contact with this surrounding adiabatic shield. For operations in the cooling mode, a constant preset temperature difference between the sample and the shield has to be maintained within the same temperature stability limits. In order to comply with these requirements in previous implementations of the ASC concept, the sample cell is suspended by thin threads inside the adiabatic shield (see for example Fig. 13.5 in Ref. [16]) and by using thermistors as highly sensitive resistance thermometers placed on the sample (holder) and on the adiabatic shield. Before these sensors can be used, time-consuming extensive calibrations (against reference thermometers) have to be executed. Moreover, the temperature coefficients of the resistance of two thermistors do never perfectly match. Via hardware adaptations in the measuring circuits [14] or via software modifications in the calibration curves, one can partly correct for this mismatch. All this made these ASC instruments complicated and they needed to be operated by a skilled and well-trained person.

In the present type of ASC [17,18], used for the results presented here, these problems are completely eliminated by inserting a very sensitive semi-conductor-material-based Peltier element (PE) between the sample and the adiabatic shield. The PE acts as a temperature difference detector and the high Seebeck coefficient of the used PE (of the order of 0.1 V K^{-1}) leads to μK sensitivity. In combination with a proper servo-system (hardware or software), this high sensitivity allows to maintain almost perfect equality of the sample and shield temperatures in the heating mode. For the cooling mode, a preset temperature difference between sample and shield can be kept constant with equal resolution. For improved shielding of ambient temperature fluctuations, additional temperature controlled shields are used.

A schematic representation of the pASC used for the results presented here is shown in Fig. 2. A small sample holder (typically $100 \mu\text{l}$) is placed in very good thermal contact on the top plate of a PE with a small heater and a miniature thermistor as a thermometer. The PE bottom plate is soldered on top of the bottom part of the surrounding thermal shield equipped with a resistive heater.

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