

MEASUREMENT OF HEAT CAPACITY BY DIFFERENTIAL SCANNING CALORIMETRY

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Abstract

The methods of measuring the heat capacity of materials by differential scanning calorimetry (DSC) are presented and discussed. The principles of temperature modulated DSC are outlined and the possibilities and limits of the method are discussed.

Key words: differential scanning calorimetry, heat capacity, temperature modulation

1 Introduction

Differential scanning calorimetry is a thermoanalytical technique, where the difference in heat flow (power) to a sample and reference is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed. DSC is the most widely used thermoanalytical technique. It enables to determine a number of parameters connected with the physical or chemical processes in condensed phase. Temperatures of phase transitions of 1. and 2. order, enthalpies of phase transitions, polymorphism in food and pharmaceuticals, liquid crystalline transitions, phase diagrams, thermoplastic polymer phase changes, glass temperatures, purity measurements and kinetic studies can be mentioned as examples where DSC is highly efficient [1,2]. DSC is very frequently used for measurement of heat capacities. This paper reviews the methods of measuring the heat capacity of materials by classical differential scanning calorimetry (DSC) and also the principles of temperature modulated DSC are outlined and the possibilities and limits of the method are discussed.

2 Determination of heat capacities by “classical” DSC

In the classical DSC, the temperature program represents a linear function of time which can be mathematically expressed as

(1)

where T is the temperature at time t , T_0 is the initial temperature and β stands for the heating rate (scan). For $\beta > 0$ the sample is heated, for $\beta < 0$ the sample is cooled and, finally, for the isothermal regime $\beta = 0$. The heat capacity is measured usually at relatively high scan rates, about 10-20 K/min. The temperature program is isotherm1-heating-isotherm2. The initial and final isotherms are measured for setting the zero value

of heat flow since if the sample is stable at constant temperature, then the heat flow to the sample is zero. The measurements are recorded in time domain.

In order to obtain reliable results, three measurements are usually carried out: the sample, the baseline and a standard. The baseline is subtracted from the sample record to obtain absolute values of the heat flow to the sample. If one takes into account eq.(1), the heat capacity can be expressed from its definition equation in the form

$$c_p = \frac{1}{m} \left(\frac{\partial H}{\partial T} \right)_p = \frac{1}{m} \left(\frac{(\partial H / \partial \alpha)}{\partial T / \partial \alpha} \right)_p = \frac{1}{m} \frac{\Delta P}{\beta}$$

(2)

where m is the sample mass, H is enthalpy and ΔP is the absolute value of the heat flow to the sample, i.e. of the DSC signal. Eq.(2) is derived using the equilibrium-thermodynamics definition of heat capacity. However, the DSC measurements are dynamic, they are not equilibrium at all. Therefore, the calibration is usually carried out by using a standard with known heat capacity (very often sapphire). A more detailed procedure can be found, for example, in paper [3].

2 Temperature modulated DSC

For temperature modulated DSC, the linear dependence of temperature on time, given by eq.(1), is modulated by a periodical function. The modulation can be sinusoidal, saw-tooth or a periodical alternation of heating-isotherm. The principle of the method can be schematically explained for the sinusoidal modulation, similarly as did it Reading in his original paper [4]. The dependence of temperature on time can thus be expressed as

$$T = T_0 + \beta t + B \sin \omega t \quad (3)$$

where B is the amplitude and ω is the angular speed of modulation.

The signals registered by the apparatus can be divided into two kinds:

- (i) signal dependent on the rate of temperature change connected mainly with the heat capacity of the sample
- (ii) signal dependent on the absolute value of temperature connected mainly with the kinetics of physical and chemical transformations.

The overall signal represents an overlap of the both signals:

$$P = c_p \frac{dT}{dt} + f(t, T) \quad (4)$$

where f is the function describing the kinetics of the transformation. If the sinusoidal modulation is considered a perturbation, then the influence of the modulation can be expressed by a Taylor series. Combination of eqs.(3) and (4) leads to the result:

$$P = c_p (\beta + B\omega \cos \omega t) + f^0(t, T) + C \sin \omega t \quad (5)$$

where f^0 is the kinetics without the temperature modulation and C is the amplitude of kinetic response.

As it can be seen from eq.(5), the registered signal represents a periodically changing dependence of heat flow on time. The signal is treated by the Fourier analysis. The cosine component is connected with the thermodynamically reversible effects of heat capacity. This component is thus called reversible. The sine component is connected with the thermodynamically irreversible kinetic effects and is called irreversible.

Hence, the temperature modulated DSC can be very efficiently used in the case when the thermodynamically reversible and irreversible processes are to be distinguished. The glass transition coupled with enthalpic relaxation is the most frequently studied example, both experimentally and theoretically [5-7]. Further, there was described the identification of glass transition in the presence of evaporating water [8], determination of heat conductivity [9], separation of reaction kinetics and phase transition [6], the heat capacity can be measured isothermally [4]. Theoretical description of the method is carried out mainly for the *heat-flux* calorimeters [4-6], less for the *power compensated* calorimeters [10]. Some further aspects are analyzed in papers [11-13] and in an almost countless number of papers published in *Thermochimica Acta* and *Journal of Thermal Analysis and Calorimetry* during the last six years.

4 Conclusions

The temperature modulated DSC can be used for the measurement of heat capacity in the cases, when an irreversible process occurs in the sample. The method offers also the measurement of heat capacity in isothermal regime, which is not possible when employing the classical DSC. The relation between the both components of DSC signal and the physico-chemical properties of materials is a very attractive field for further research.

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