Multifunctional Device For Measuring Thermal Properties Under Phase Transitions

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Abstract. In this article a new multifunctional device is considered. This device enables simultaneous measurement of thermal properties such as enthalpy, effective thermal capacity, melting point, differential and integral heat of phase transitions, initial moisture content and some other heat and humidity characteristics of the materials and food products at different temperature levels. Theoretical analysis of this device is based on a well-known principle of “regular regime”. The theoretical model of the device and the formulas for determining different thermal properties are given in this article.

1. Introduction

It is well known that thermophysical properties of the substances greatly depend on their chemical composition, internal structure and environmental conditions. Therefore the theoretical calculation of thermophysical properties is very difficult. In this case only experiment could be the most powerful tool for making accurate calculations of such properties. To solve this problem has been the main aim of the scientists headed by Prof. Evgeniy Platumov during the last 50 years [4]. As a result the theoretical basement of non-linear monotic regime method has been developed. This method underlies the operation of many devices that has been developed [1-3]. These devices are intended for measurement thermophysical properties in the temperature range from 4.2 K to 2000 K. This method also enables simultaneous measurement of enthalpy, effective thermal capacity, differential and integral heat of phase transitions, initial moisture content and some other heat and humidity characteristics of the materials and food products at different temperature levels. The rapid development of electronics in the last 30 years, led to improvement of the techniques that are used in modern thermophysical experiments and which made it possible to do an automatization of such experiments. The automated device is considered in this article.

Under conditions of cooling and heating of moisture-containing substances in the area of crystallization, intense thermal effects of phase transitions of bound moisture are observed. Phase transitions act inside the sample as heat sources, the intensity of which in unsteady conditions is a complex function of temperature. These internal heat sources strongly influence the enthalpy, temperature field and, as a consequence, the heat treatment of the sample at all stages of its cooling and heating.

2. Theoretical Background

Thus, the unsteady heat equation for samples in the field of crystallization of bound water acquires a purely nonlinear form [5]

$$\text{div}\left[\lambda(t) \text{ grad}\right] = \left[ c(t) + w(t) \right] \rho \frac{\partial t}{\partial t},$$  

(1)

where $t = t(x, y, z, \tau)$ – temperature field of the sample; $\lambda(t)$ – thermal conductivity; $c(t)$ – heat capacity of single-phase product components; $w(t) = dh_{nb}(t)/dt$ – temperature derivative of specific enthalpy $h_{nb}(t)$ of phase transformations in the product. Temperature derivative of specific enthalpy characterizes the density of the temperature distribution of the integral specific heat of melting of the water in the product $q_m$ and is functionally related to the $q_{in}$

$$q_m = \int w(t) dt.$$  

(2)

Integrate equation (1) over the entire volume of the sample $V$. After integration, the left side of the equation determines the total heat flux $Q(t)$, that flows to the sample from the outside through the outer surface. Therefore, instead of equation (1), it is possible to write the equation of the thermal balance of the sample with an external heat source.
\[ Q(t) = \int (c+w) \rho \frac{\partial^2 T}{\partial T^2} \ dV. \]  

Equation (3) is significantly simplified if the sample is homogeneous, and the experiment is carried out in conditions under which the temperature field of the sample is maintained uniform throughout its volume. In this case, the integrand function ceases to depend on the coordinates (volume) and equation (3) takes the form

\[ Q(t) = \int (c(t)+w(t)) \rho V \frac{\partial^2 T}{\partial T^2}. \]  

This equation serves as a theoretical basis for the proposed method of studying the thermal and humidity characteristics of samples in a wide temperature range, including the crystallization of bound moisture.

A preliminary mathematical analysis has shown that in different modes of freezing or thawing of the samples, the uneven temperature field should not exceed a few tenths of a Kelvin. In practice, this means that measurements should be carried out on samples of small size, since only under these conditions it is possible to significantly intensify the external thermal effects on the sample and reduce the duration of the experiment to 20...30 minutes, maintaining a fairly uniform temperature field inside the sample.

Studies of various substances have shown that with such a duration of experiment, the influence of thermal effects due to chemical and structural transformations in the sample can be neglected, and the thermal effects of phase transformations of bound water, which are unambiguous functions of temperature, become decisive. Due to this, to characterize the thermal properties of samples in the field of crystallization are often limited to the concept of effective heat capacity \( c_{eff}(t) = c(t) + w(t) \). However, there is a principal possibility of determining separately the true specific heat of the initial components of the product \( c(t) \) and the differential heat of melting of the bound water \( w(t) \).

3. Experimental Setup

The component parts of device are calorimetric unit for measuring humidity and heat characteristics of samples with the volume of 4...5 sm³ in the temperature range –30...20 °C and electronic-computing unit (controller). The controller provides primary gathering and processing of experimental information and digital readout of the results of the experiment. It allows executing the data transfer to a personal computer for further processing with the help of the present software in MS Origin, Mathcad. Physical model of the device is shown on Figure 1. In the center of the massive metal unit (4) is a cylindrical cavity with the foam plastic cylindrical layer (3) tightly inserted into it. The measurement of heat capacity and enthalpy a cell with six blind holes (2) is used. These blind holes are filled by the sample (1). The cell with sample is placed into the cavity of the unit where the microthermistor is installed. This microthermistor is set inside the cell and provides the measurement of sample temperature \( t_s \). There is an additional microthermistor for the registration of temperature in the metal unit \( t_m \).

Filled in before the experiment, the cell is cooled to the given low temperature by any means. The cell, prepared for the experiment, is quickly inserted into the metal unit. After that the cell begins to be warmed by the heat flow coming to it from the unit through the foam plastic layer. The controller registers, with a given temporal step (1...20) sec, the indication of the microthermisters, thus creating the necessary set of the experimental points. The experimental information about the temperature curves is used for the calculation enthalpy of the studied matter as a function of temperature:

\[ h[t_m, t_s] = \frac{1}{M} \int_0^T K_s(t_s) \left[ t_s(t) - t_s(\tau) \right] d\tau = \left( C_s(t_s) + \frac{5}{16} C_s(t_s) \right) \left[ t_s(\tau) - t_s(t) \right]. \]  

Parameters \( K_s \) and \( (C_s + 5C_s/16) \) are defined by the thermal conductivity and heat capacity of the foam plastic layer and cell. The calibration of a layer is executed during the experiments with the cell specially made of the metal the heat capacity of which is well known and also with the empty cell.

Effective thermal capacity can be determined as:
\[ c_{\text{ef}}(t) = \frac{d}{dt} h(t_0, t). \]  

The cryoscopic temperature \( t_c \) is identified with the maximum temperature on the curve of the effective heat capacity of the product \( c_{\text{ef}}(t) \). The proportion of frozen water at different temperature levels \( \omega(t) \), measured from the total mass of the product, can be calculated using the expression

\[ \omega(t) = 1 - \frac{h_{\text{th}}(t)}{L}, \]

where \( h_{\text{th}}(t) \) - specific enthalpy of phase transition; \( L \) – specific heat of melting (crystallization) of distilled water.

The procedure of the experiment and treatment of its results is completely automated. It allows studying the kinetics of the phase transition in all kinds of materials both in solid and liquid states during their freezing and thawing. The duration of experiment does not exceed half an hour. This device allows studying effective thermal capacity with fractional error better than 4…5%.

**Figure 1.** Physical model of the device for measuring humidity and heat characteristics

4. Experimental results and discussions

Using the described method and the calorimeter we measured thermophysical properties of several dozens of materials of different origin and structure. Special attention was paid to the temperature field of phase transitions.

As an example, Figure 2 shows the experimental dependence of the specific enthalpy NaCl as a function of temperature, obtained by using the relation (5). For the start of the reference enthalpy adopted temperature \( t = 0^\circ\text{C} \). The enthalpy of aqueous solution obtained at the different concentration from 5 to 35%. Figure 3 shows the temperature dependences of the effective specific heat capacities for salt solutions, that was calculated by equation 6.

As well known, for most moisture-containing materials, the heat capacity outside the zone of phase transitions is weakly dependent on temperature. Because the moisture content in solutions can reach 35%, the chart is well visible the phase transition water-ice.
The presented graphs clearly demonstrate the fact that the change in the concentration of the solution leads to a change in the cryoscopic temperature. The change in concentration of almost six times leads to the fact that the cryoscopic temperature has changed from -3°C to -21°C. Moreover, in this case the phase transition is significantly stretched over the temperature range.

Thus, from the graphs for enthalpy it is possible to obtain the temperature dependence on specific heat and moisture content of the sample. Our results obviously demonstrate fact that it is necessary to know not only the integral quantitative values of thermophysical properties, but their functional dependence on temperature of the researched object.

Figure 2. The enthalpy of aqueous solution of NaCl as a function of temperature at the different concentration

Figure 3. The heat capacity of aqueous solution of NaCl as a function of temperature at the different concentration

5. Conclusions

Thus, we proposed method of investigation of various materials under the conditions of freezing and melting when the material is undergoing the intensive phase and structural transitions. This method allows studying the
kinetics of the changes of the thermophysical characteristics of materials, as in the mode of monotonic heating and freezing of the samples. Using this method we created a calorimeter which can measure enthalpy and heat capacity as a function of temperature in the temperature range from -30°C to 20°C.

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