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BRIEF MEASUREMENTS OF THERMAL ACTIVITY IN THE MELTING

RANGE OF A SUBSTANCE

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Methodological features of brief measurements in the phase transition region are examined.

It is known that the abrupt character of fusion, which is characterized by an infinitely small temperature range, is an idealization which corresponds only to perfect crystal structures. In actual polycrystalline systems — especially high-molecular-weight systems [1] — in real crystallization periods, complete thermodynamic equilibrium is not achieved, and the chemical potentials of the systems depend on other factors besides temperature and pressure. Among these factors are the degree of ordering and the size of the crystallite. This situation appreciably broadens the temperature range in which melting occurs; sometimes the range is quite large (about 10°C).

The interpretation of results of nonsteady thermophysical experiments conducted in this range is not always unambiguous.

The measurement process is significantly affected by absorption of heat of fusion during a change in the phase of a substance and the temperature dependence of its thermophysical characteristics. Also, for the brief measurements [2] we are discussing — when the measurement time is 10^{-4} sec — the kinetics of fusion should be taken into account.

The propagation of the temperature field in a substance undergoing a phase transition is connected with the appearance of heat sinks, the capacity of which is proportional to the fraction of melted substance and the heat of fusion h.

Let the content of the liquid phase in the melting range be given by the function $u(T, t)$. In the general case, this function depends both on temperature and, explicitly, on time. The latter fact is related to the kinetics of fusion. In particular, a "lag" in the development of fusion relative to the melting point was noted in [3] for polyethylene glycol (PNG). The size of the "lag" depends on the molecular weight and in the case of PNG is on the order of 10^{-3}–10^{-2} sec. Without concerning ourselves with the mechanism of the lag, to describe it we naturally determine the concentration of the liquid phase in the form

$$u(T, t) = u_0(T) \left(1 - \exp\left(\frac{t}{\tau}\right) \right),$$ (1)

where τ is the relaxation time, a parameter which quantitatively determines the lag.

With allowance for (1), we will write the expression for the unit capacity of volumetrically distributed heat sinks as $\omega = h \dfrac{\partial u}{\partial T} \dfrac{\partial T}{\partial t}$. Accordingly, the model problem describing the measurement process takes the form

$$\rho_1 c_1 \frac{\partial T_1}{\partial t} - \lambda_1 \frac{\partial^2 T_1}{\partial x^2} = 0, \quad x < 0, \tag{2}$$

$$\rho_2 c_2 \frac{\partial T_2}{\partial t} - \frac{\partial}{\partial x} \left(\lambda_2 \frac{\partial T_2}{\partial x} \right) = h \frac{\partial u(T_2, t)}{\partial T_2} \frac{\partial T_2}{\partial t}, \quad x > 0$$

with the initial conditions

$$T_1(x, 0) = T_2(x, 0) = 0 \tag{3}$$

and boundary conditions

$$T_1(-\infty, t) = 0, \quad T_2(\infty, t) = 0,$$

$$\lambda_1 \frac{\partial T_1}{\partial x} - \lambda_2 \frac{\partial T_2}{\partial x} = q_0 \quad \text{at} \quad x = 0, \tag{4}$$

$$T_1 = T_2 \quad \text{at} \quad x = 0.$$

We will assume that the parameters of the investigated medium are linearly dependent on temperature:

$$\lambda_2 = \lambda_{20}(1 + \alpha T), \quad \rho_2 c_2 = \rho_{20} c_{20}(1 + \beta T).$$

The problem formulated is a mathematical model for the process of measuring thermal activity, characterized by duration t and the amount of heating T(x, t). Here, we consider the absorption of heat of the phase transition, the kinetics of the process, and the temperature dependence of the thermophysical characteristics of the substance. In the general case, it is difficult to find an analytic solution, and numerical methods must be used. However, analytic methods are possible with both long and short measurement times. We will examine several cases.

1. For $t \gg \tau$ (long measurement time), u(T, t) = u_0(T) and system (2) takes the form

$$\rho_1 c_1 \frac{\partial T_1}{\partial t} - \lambda_1 \frac{\partial^2 T_1}{\partial x^2} = 0, \quad x < 0, \tag{5}$$

$$[\rho_{20} c_{20}(1 + \beta T_2) - k] \frac{\partial T_2}{\partial t} - \frac{\partial}{\partial x} \left(\lambda_{20}(1 + \alpha T_2) \frac{\partial T_2}{\partial x} \right) = 0, \quad x > 0,$$

where k = h du_0/dT = const. (This assumption is valid for a small amount of heating during measurement).

The second equation in (5) is quasilinear. We will represent T_1 and T_2 in the form of series:

$$T_1(x, t) = T_{10}(x, t) + T_{11}(x, t) + \ldots; \quad T_2(x, t) = T_{20}(x, t) + T_{21}(x, t) + \ldots \tag{6}$$

Having inserted (6) into (5) and having equated the terms of the same order, we obtain the system for the first approximation

$$\frac{\partial T_{10}}{\partial t} - a_1 \frac{\partial^2 T_{10}}{\partial x^2} = 0, \quad a_1 = \frac{\lambda_1}{\rho_1 c_1}, \tag{7}$$

$$\frac{\partial T_{20}}{\partial t} - a_2 \frac{\partial^2 T_{20}}{\partial x^2} = 0, \quad a_2 = \frac{\lambda_2}{\rho_{20} c_{20} - k}$$

with the initial and boundary conditions

$$T_{10} = T_{20} = 0 \quad \text{at} \quad t = 0, \ |x| \to \infty,$$

$$T_{10} = T_{20}, \quad \lambda_1 \frac{\partial T_{10}}{\partial x} - \lambda_{20} \frac{\partial T_{20}}{\partial x} = q_0 \quad \text{at} \quad x = 0.$$

The solution of system of linear equations (7) is known [4]:

$$T_{10} = \frac{2 q_0 \sqrt{t}}{\varepsilon_1 + \varepsilon_{ef}} \text{ierfc} \left(-\frac{x}{2 \sqrt{a_1 t}} \right), \tag{8}$$

$$T_{20} = \frac{2 q_0 \sqrt{t}}{\varepsilon_1 + \varepsilon_{ef}} \text{ierfc} \left(\frac{x}{2 \sqrt{a_2 t}} \right), \tag{9}$$

where

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$$\varepsilon_1 = \sqrt{\rho_1 c_1 \lambda_1}, \quad \varepsilon_{\text{ef}} = \sqrt{\rho_{20} c_{20} \lambda_{20}} \sqrt{1 - \frac{k}{\rho_{20} c_{20}}} = \varepsilon_2 p;$$

$$\varepsilon_2 = \sqrt{\rho_{20} c_{20} \lambda_{20}}; \quad p = \sqrt{1 - \frac{k}{\rho_{20} c_{20}}}.$$

We write the system for the second approximation:

$$\frac{\partial T_{11}}{\partial t} - a_1 \frac{\partial^2 T_{11}}{\partial x^2} = 0, \tag{10}$$

$$(\rho_{20} c_{20} - k) \frac{\partial T_{21}}{\partial t} - \lambda_{20} \frac{\partial^2 T_{21}}{\partial x^2} = \frac{1}{2} \left(\lambda_{20} \alpha \frac{\partial^2 T_{20}^2}{\partial x^2} - \rho_{20} c_{20} \beta \frac{\partial T_{20}^2}{\partial t} \right), \tag{11}$$

$$\text{at} \quad t = 0 \quad T_{11} = T_{21} = 0,$$

$$\text{at} \quad x = 0 \quad T_{11} = T_{21},$$

$$\lambda_1 \frac{\partial T_{11}}{\partial x} - \lambda_{20} \frac{\partial T_{21}}{\partial x} = -\gamma \sqrt{t},$$

where $\gamma = 2q_0^2 \alpha \lambda_{20} / \sqrt{\pi a_2} (\varepsilon_1 + \varepsilon_{\text{ef}})^2$.

Linear equation (10) with boundary conditions of the second type $\partial T_{11}/\partial x \sim \sqrt{t}$ has a solution of the form

$$T_{11}(x, t) = A \cdot 2\sqrt{a_1 \pi} \, t \, i^2 \text{erfc}\left(-\frac{x}{2\sqrt{a_1 t}} \right), \tag{12}$$

where A is a constant. From here we obtain the boundary condition for (11)

$$\frac{\partial T_{21}}{\partial x} = \frac{\sqrt{t}}{\lambda_{20}} (\lambda_1 A + \gamma) = \varphi(t). \tag{13}$$

Using (9), we rewrite (11) in the form

$$\frac{\partial T_{21}}{\partial t} - a_2 \frac{\partial^2 T_{21}}{\partial x^2} = \frac{\alpha r}{4} \text{erfc}^2 \left(\frac{x}{2\sqrt{a_2 t}} \right) + \frac{r}{2\sqrt{\pi}} \left(\alpha - \frac{\beta}{p^2} \right) \exp \left(-\frac{x^2}{4a_2 t} \right) \text{ierfc}\left(\frac{x}{2\sqrt{a_2 t}} \right) = h(x, t), \tag{14}$$

where $r = 4q_0^2 / (\varepsilon_1 + \varepsilon_{\text{ef}})^2$. The solution of (14), with boundary condition (13), is known [5]:

$$T_{21}(0, t) = -\sqrt{\frac{a_2}{\pi}} \int_0^t \frac{\varphi(\tau) \, d\tau}{\sqrt{t - \tau}} + \frac{1}{\sqrt{a_2 \pi}} \int_0^t \frac{d\tau}{\sqrt{t - \tau}} \int_0^\infty h(\xi, \tau) \, d\xi =$$

$$= -\frac{\lambda_1 A + \gamma}{2\lambda_{20}} \sqrt{a_2 \pi} \, t + \frac{\alpha r t}{4} \left(1 - \frac{2}{\pi} \right) + r \left(\alpha - \frac{\beta}{p^2} \right) \frac{t}{16}. \tag{15}$$

Using the boundary conditions, we have:

$$A = \frac{q_0^2}{\sqrt{a_1 \pi}} \frac{\varepsilon_{\text{ef}}}{(\varepsilon_1 + \varepsilon_{\text{ef}})^2} \left(\alpha \left(\frac{1}{2} - \frac{4}{\pi} \right) - \frac{\beta}{2p^2} \right).$$

Accordingly

$$T_{21}(0, t) = \frac{q_0^2 t}{\pi (\varepsilon_1 + \varepsilon_{\text{ef}})^2} \left(\alpha \left(\frac{\pi}{4} - 2 \right) - \frac{\beta}{p^2} \frac{\pi}{4} \right) \frac{\varepsilon_{\text{ef}}}{\varepsilon_1 + \varepsilon_{\text{ef}}} =$$

$$= T_{20}^2(0, t) \left(\alpha \left(\frac{\pi}{16} - \frac{1}{2} \right) - \frac{\beta}{p^2} \frac{\pi}{16} \right) \frac{\varepsilon_{\text{ef}}}{\varepsilon_1 + \varepsilon_{\text{ef}}}.$$

Thus,

$$T_2(0, t) = T_{20}(0, t) + T_{20}^2(0, t) \left(\alpha \left(\frac{\pi}{16} - \frac{1}{2} \right) - \frac{\beta}{p^2} \frac{\pi}{16} \right) \frac{\varepsilon_{\text{ef}}}{\varepsilon_1 + \varepsilon_{\text{ef}}}.$$

This expression determines the empirically measured temperature of a low-inertia heater heated by rectangular current pulses. The effect of the heat capacity of the heater itself, not considered in problem (2), was examined in [6]. In the case of a small amount of heating (for values of the coefficients α and β in the phase transition region equal to 10^{-1} K^{-1}, the heating should be on the order of 10^{-1} K), we have:

$$T_2(0, t) \approx T_{20}(0, t) = \frac{2q_0 \sqrt{t}}{\sqrt{\pi} (\varepsilon_1 + \varepsilon_{\text{ef}})}. \tag{16}$$
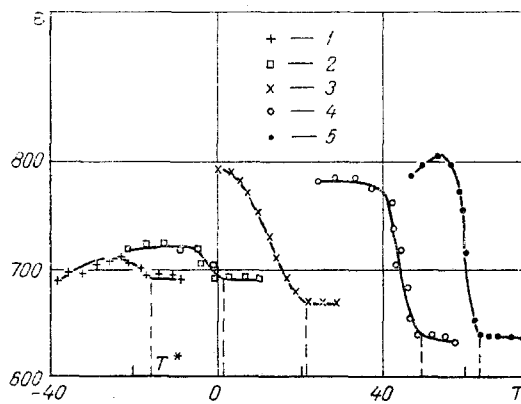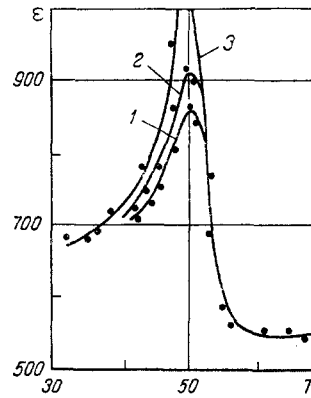
Fig. 1. Thermal activity of polyethylene glycol in the melting range: 1) PNG-300; 2) PNG-400; 3) PNG-600; 4) PNG-200; 5) PNG-6000; T* is the melting point; the points denote empirical results, while the curves represent smoothed functions.

Fig. 2. Dependence of the thermal activity of diphenylamine on pulse duration: 1) 200 μsec; 2) 400 μsec; 3) 700 μsec; the points denote empirical results, while the curves represent smoothed functions.

2. We will further examine the case of short heating times. For $t \ll \tau$, Eq. (2) takes the form

$$\frac{\partial T_1}{\partial t} - \lambda_1 \frac{\partial^2 T_1}{\partial x^2} = 0, \quad x < 0,$$

$$\rho_{20} c_{20} (1 + \beta T_2)] \frac{\partial T_2}{\partial t} - \frac{\partial}{\partial x} \left(\lambda_{20} (1 + \alpha T_2) \frac{\partial T_2}{\partial x} \right) = 0, \quad x > 0.$$

Using (9) and (15) and considering that k = 0, we obtain

$$T_2(0, \ t) = \frac{2q_0 \sqrt{t}}{\sqrt{\pi} (\varepsilon_1 + \varepsilon_2)} + \frac{q_0^2 t}{\pi (\varepsilon_1 + \varepsilon_2)^2} \left(\alpha \left(\frac{\pi}{4} - 2 \right) - \beta \frac{\pi}{4} \right) \frac{\varepsilon_2}{\varepsilon_1 + \varepsilon_2}. \tag{17}$$

Accordingly, with a small amount of heating

$$T_2(0, \ t) \approx \frac{2q_0 \sqrt{t}}{\sqrt{\pi} (\varepsilon_1 + \varepsilon_2)}. \tag{18}$$

Thus, it follows from the above analysis that at $t \gg \tau$ the measured value will be the effective thermal activity ε_{ef}; at $t \ll \tau$, the measured value is the true thermal activity. This is physically related to the fact that the temperature field propagates over the investigated region so quickly that melting does not have time to develop. Such measurements can be used to study the actual heat capacity in the melting range. It is almost impossible to determine by traditional calorimetric methods due to thermal effects accompanying the phase transition. When t ∿ τ, the result of measurement of thermal activity depends on the measurement time.

Figures 1 and 2, respectively, show results of thermal activity in the melting range of polyethylene glycol with different molecular weights and diphenylamine. The results were obtained using the method examined in [6]. The duration of the measurement pulse in the study of polyethylene glycol was 200 μsec, while pulses of three durations were used in studying diphenylamine: 200, 400, and 700 μsec.

The experimental results clearly reflect the nonequilibrium character of melting. In particular, polyethylene glycol is characterized by the absence of a maximum in the relation ε(T), which permits us to classify the study results as the true thermal activity, undistorted by thermal effects.

The case when t ∿ τ is realized for diphenylamine, and the kinetics of the melting process affect the measurements of thermal activity.

NOTATION

$u(T, t)$, content of liquid phase, kg/kmole; ρ, density, kg/m^3; c, heat capacity, J/kg·K; λ, thermal conductivity, W/m·K; x, coordinate, m; t, time, sec; $T(x, t)$, temperature, °K; τ, relaxation time, sec; ε, thermal activity, J/m^2·K·sec$^{1/2}$. Indices: 1) substrate; 2) test medium.

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DETERMINATION OF THE TRUE THERMAL CONDUCTIVITIES OF HELIUM AND NITROGEN AT ATMOSPHERIC PRESSURE AND TEMPERATURES FROM THE NORMAL BOILING POINTS TO 6700°K

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True values of the thermal conductivity of helium are calculated and the data obtained is compared with theoretical values and available generalized data on thermal conductivity.

The studies [1-64]* present data on the thermal conductivity of helium measured in the temperature range 3.3-6700°K at atmospheric pressure (Table 1). There is a substantial difference among the experimental results obtained both by different methods and by the same methods with identical state parameters of the gas. The goal of the present study is to obtain generalized data on the thermal conductivity of helium measured by steady-state methods — plane layer, hot-wire, and column — and by transient methods — shock tube and hot-wire.

The first four methods belong to the same group, which is characterized by the fact that a density gradient occurs in the measuring device while the pressure of the test gas remains constant.

The transient hot-wire method belongs to another group which is characterized by the occurrence of a pressure gradient in the measuring device while the density remains constant. It should be noted that this method has not yet come into wide use because it can be used to measure thermal conductivity only within a narrow temperature range (300-400°K) at high pressures.

As was shown in [67], energy transfer occurs under the conditions of experiments conducted by methods of the first group as a result of temperature and density gradients. In this case, the relationship between the true thermal conductivity (the value which character-

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.*The first studies of the thermal conductivity of helium were reported in [65, 66].