NOTATION

ρ, density; v, velocity; p, pressure; T, temperature; τ, density of the mass flow; Σ, density of impulse flow; q, density of heat flow; h, enthalpy; λ', effective coefficient of thermal conductivity; σ, surface-tension coefficient; v_1, v_2, v_3, rates of change of the coordinates x_1, x_2, x_3, respectively; $\bar{u}_1$, $\bar{u}_2$, average velocities of liquid in front of the first meniscus and column of liquid, respectively; $\bar{v}_1$, $\bar{v}_2$, velocities of vapor in the vapor plug and at the exit from the capillary; α, condensation coefficient; μ, molecular weight; R^*, universal gas constant; P(T), saturated vapor pressure at the temperature T; λ_v, λ_l, $\lambda_{p.m}$, coefficients of thermal conductivity of vapor, liquid, and material of the porous matrix.

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COMBINED MEASUREMENT OF THERMAL PROPERTIES OF FLUIDS

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A dilatometric method for simultaneous determination of the heat capacity and the coefficient of thermal expansion of fluids is described.

Rapid dilatometric methods for the determination of the thermal diffusivity of materials [1], which have demonstrated undisputed advantages in the study of heat-transfer parameters [2], can be used as a means for combined measurement of the properties of thermal expansion and heat capacity in fluids [3].

Among the principal proposals for such an expansion in the area of application of dilatometry (while preserving such important qualities as the nondestructive and highly accurate nature of the method, which is not based on measurement of temperatures and thermal fluxes in test objects), one should consider the comparative version involving thermal change in the volume of two fluids – a standard (with known values for the volumetric heat capacity c_0 and for the coefficient of thermal expansion β_0) and a test fluid (the thermophysical characteristics c_T and β_T of which are subject to determination) – under conditions where the variation of heat content in each of them occurs only because of heat exchange through a boundary separating the fluids (a thin nondeformable shell).

As a specific model for the realization of the method, it is convenient to select a system of two "imbedded" thin-walled metal vessels made of a material with a negligibly small coefficient of thermal expansion in comparison with the same parameter for the fluids. The fluid with standard properties fills the outer vessel 1 (Fig. 1) in such a way that the inner vessel 3 is completely immersed in the standard fluid, which is in

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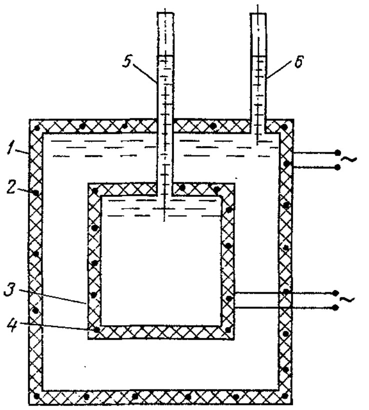

Fig. 1

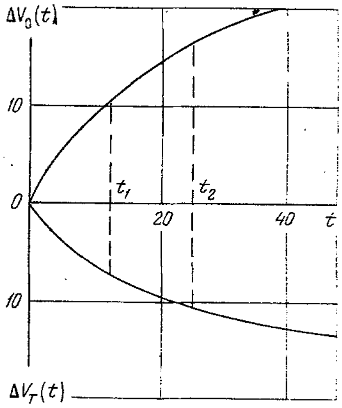

Fig. 2

Fig. 1. Block diagram of dilatometer.

Fig. 2. Kinetic curves for volumetric thermal expansion $\Delta V_0(t)$ of a standard fluid and $\Delta V_T(t)$ of a test fluid because of heat exchange through a thin shell separating them (t is time measured from the moment the inner heater is turned off).

contact with the entire external surface of 3. The role of driving force for expansion of both fluids is assigned to electrical heating which is initiated by the electrical heater 4 mounted within the shell separating the volumes of the inner and outer vessels. The initial departure of the system from thermal equilibrium is produced by a short power pulse in the heater 4.

Temperature perturbations in both fluids after this heater is shut off involve only the regions adjacent to it and the kinetics of thermal expansion in each of the fluids depends only on the heat exchange between them through the shell 3. Observation of the kinetic details of the thermal expansion of both fluids is accomplished by means of the measuring tubes (capillaries) 5 and 6 fitted on the outer and inner vessels. It is pertinent to emphasize that filling of the capillaries with the fluids is by no means a necessary part of the experiment; for example, it is completely satisfactory to have capillaries made of glass and a drop of fluid that does not wet glass (in particular, mercury) located halfway up each of them. The buffer region of gas (air) formed in this way between the surface of the fluids and the mercury drops in the capillaries is extremely favorable in two respects at the same time: first, by reducing parasitic heat transfer to the surroundings and, second, by relieving the experimenter of the need to fill the capillaries with the fluids (which is frequently difficult from the operational aspect if the test fluid is a highly viscous material).

The geometric sizes of the capillaries were chosen so that insignificant changes in the volumes of the fluids produced displacements of the mercury drops that were noticeable under visual observation. It is obvious that the visibility of observations in this case does not eliminate automatic recording of the kinetics of fluid expansion, for example, by noninertial (fast-writing) recorders.

The features of heat exchange between the standard and test fluids are such that cessation of thermal expansion by one of them does not mean cessation of volumetric changes in the other. Along with this, the absence of thermal expansion of the fluid in the inner vessel is evidence that the total thermal flux through the shell 3 has become zero. To eliminate the effect of heat exchange between the outer vessel and the surroundings, the additional electrical heater 2 is provided, which is combined with the outer shell 1 of the outer vessel.

During heat exchange between the two fluids, time and coordinate nonuniformities of the temperature fields in both vessels arise and it therefore makes sense to follow the previously proposed line of reasoning [2] in calculating the behavior of the thermal expansion of one or the other of the fluids. In particular, neglecting thermal deformation of the walls of the vessels (which is facilitated by the extremely small amount of material in the walls as compared to the amount in the fluids), it is proper to consider the change in volume d^2V_T of an infinitely small volume element dV of a fluid (of the test fluid, for example) in the infinitesimal time dt:

$$d^2V_T = \beta_T dV \frac{\partial T}{\partial t} dt, \tag{1}$$

where $\partial T/\partial t$ is the instantaneous value of the temperature rate of change at the location of the selected fluid element dV [2].

If the maximum temperature drop in the fluid at each moment of the procedure is such that there is no effect on the temperature dependence of the parameters β_T and c_T, the total value of the rate of thermal expansion W_T for the entire volume V of the fluid is calculated from the obvious transformation of the initial equation (1):

$$W_T = \frac{dV_T}{dt} = \beta_T \int_0^V \frac{\partial T}{\partial t} dV. \tag{2}$$

Subsequent calculations are based on the use of the known equation of thermal conductivity, which in the absence of heat sources within the fluid contains the coefficient of thermal conductivity λ along with the heat capacity c_T [4],

$$c_T \frac{\partial T}{\partial t} = \operatorname{div} (\lambda \operatorname{grad} T). \tag{3}$$

Transforming the volume integral in Eq. (2), after substitution in it of the value of $\partial T/\partial t$ from Eq. (3), into the integral of the flux field q over the surface S by means of the Ostrogradskii–Gauss theorem [5], it is easy to obtain a simple formula for calculation of the rate of expansion W_T:

$$W_T = \frac{\beta_T}{c_T} \int_0^S q dS. \tag{4}$$

Under conditions of heat exchange between the fluids where the change in the heat content of each of them occurs because of heat transfer through the surface S separating them, the rate W_0 of the thermal expansion of the standard fluid is also proportional to the integral in Eq. (4) taken with a minus sign and to the ratio of the parameters β_0 and c_0:

$$W_0 = -\frac{\beta_0}{c_0} \int_0^S q dS. \tag{5}$$

The observed property of thermal expansion of the fluids because of heat exchange between them is not only seen with a thermally insulated (adiabatic) outer shell 1, but also in the very initial stages of breakdown in thermal equilibrium between the two fluids occurring at the boundary 3 and particularly when the temperature of the fluid near the outer shell 1 is the same as the temperature of the shell while the temperature of the fluid in the inner vessel is different. Disregarding the contribution from thermal deformation of the heaters (and of the vessel walls) to the thermal expansion of the fluids (the coefficient of thermal expansion for the solid phase materials is ordinarily two or three orders of magnitude less than that for the fluids [6]) and then operating only with absolute values of the rates W_0 and W_T, it is easy to obtain from Eqs. (4) and (5)

$$W_0 = W_T \frac{c_T}{c_0} \cdot \frac{\beta_0}{\beta_T}. \tag{6}$$

It is easy to observe that for a certain rate of heat release in the outer heater 2, an equilibrium condition sets in when the inner heater 4 is turned off, i.e., all the power released in heater 2 is consumed in compensating for heat losses to the surroundings. At equilibrium, obviously, thermal expansion of the fluids stops and there are no temperature gradients in their volumes. Thereby, the value of the temperature rise ΔT for each of the fluids coincides for an identical (constant) initial temperature of the two. Consequently, multiplying the numerator and denominator of the fraction in Eq. (6) by ΔT and considering that

$$\Delta T \beta_{T,0} = \frac{\Delta V_{T,0}}{V_{T,0}}, \tag{7}$$

where ΔV_T and ΔV_0 are, respectively, the absolute increases in the volumes of the test and standard fluids, the initial volumes of which are V_T and V_0, we arrive at a final computational formula for determining the volumetric heat capacity c_T of the test fluid:

$$c_T = c_0 \frac{W_0}{W_T} \cdot \frac{\Delta V_T}{\Delta V_0} \cdot \frac{V_0}{V_T}, \tag{8}$$

which does not require data from measurements of temperatures and thermal fluxes in the fluids.

By periodically repeating the alternating thermal effect on the system through both heaters (a pulsed effect by means of the inner heater and through an increase in electrical power in the outer heater for a shift in the equilibrium heat release), it is not difficult to carry out a continuous study of the temperature behavior of heat capacity and of the coefficient of thermal expansion for the test fluid.

The high overall accuracy of the method (the relative error in measurements of absolute linear expansions during identical time periods is no more than 0.3-0.5% so that the total error of the method can be reduced to 0.5-1.5% without special effort) is furthered by the fact that recording of the rates W_0 and W_T can be replaced by measurement of the absolute increases in volume $\Delta V_0(t_1)$ and $\Delta V_T(t_1)$ during the same time t_1.

In fact, it is simple to confirm the validity of the important property

$$\frac{W_0}{W_T} = \frac{\Delta V_0(t_1)}{\Delta V_T(t_1)} = \frac{\Delta V_0(t_2)}{\Delta V_T(t_2)} \tag{9}$$

by integrating both sides of Eq. (6) with respect to time over the interval t_1 or t_2.

Among other advantages of the method, one should mention that the derivation of Eq. (8) did not require limitation to any specific boundary or initial conditions determining the form of one or another solution of the equation of thermal conductivity (3).

In addition, the specific form of Eq. (8) makes it possible to calculate the heat capacity c_T directly from experimental curves for $\Delta V_0(t)$ and $\Delta V_T(t)$ plotted by fast-writing recorders (in the present work, an N-327-5 recorder) in an arbitrary scale of units without bringing in information about the design constants of the amplification system or of the equipment for automatic recording of the kinetic curves for expansion of the fluids. In fact, considering the property (9) cited, all design constants to which the recorded signal containing the quantities ΔV_T and $\Delta V_T(t_1)$ [the quantities ΔV_0 and $\Delta V_0(t_1)$ also] in the form of the ratio of these parameters in Eq. (8) is proportional are cancelled out, which considerably simplifies the analysis of the experimental data.

The method described above was used to study the properties of analine in the temperature range 20-60°C. Glycerine, with a known volumetric heat capacity of 0.72 cal/deg · cm^3 [6], was selected as the standard fluid. The typical form of the kinetic thermal expansion curves for both fluids is shown in Fig. 2 in the stage of heat exchange through a thin-walled glass shell separating them.

Windings of Nichrome wire acting as electrical heaters (see Fig. 1) were pressed into both the outer and inner shells (1 mm thick). The shape of both vessels was chosen to be cylindrical with the height of the vessels being 10 and 5 cm, respectively, and the diameters being 10 and 6 cm.

For measuring tubes (glass capillaries) 40 cm long, the diameter of each was 1 mm. The drop of mercury displaced in the capillaries shorted two platinum wires, which changed the resistance in an electrical circuit. The electrical signal from the wire detector was fed to the input of an N-327-5 recorder.

The measured value for the volumetric heat capacity of analine at a temperature of 40-50°C was 0.52 cal/deg · cm^3, which is in good agreement with known data [6].

NOTATION

β, coefficient of thermal expansion; λ, coefficient of thermal conductivity; c, heat capacity of material per unit volume; q, thermal flux; t, time; V, volume; S, surface; T, temperature; W, rate of thermal expansion of samples.

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