

SPECIFIC HEAT OF LIQUIDS AT CONSTANT PRESSURE
 INVESTIGATED BY THE METHOD OF CONTINUOUS
 HEATING IN THE QUASIREGULAR REGIME

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The essence of the method consists in comparing the heating curves of the test liquids and a standard liquid. The method was first proposed by Osmond for investigating internal transformations in solids [1]. Later on, it was used by Turovskii and Bartenev [2] to investigate the specific heat of metals. In the Tur-
 ofskii-Bartenev apparatus two samples, of exactly the same size and shape, of the investigated and standard (of known specific heat) metals with a blackened surface were cooled under identical conditions (in the open air). The dependence of the temperatures of both specimens on time was recorded, and the specific heat of the test specimen C_1 was found from the formula

$$C_1 = C_2 \frac{G_2 (dt/d\tau)_2}{G_1 (dt/d\tau)_1} \quad (1)$$

Here, C_2 and G_2 are the specific heat and weight of the standard material, G_1 is the weight of the test specimen, t is temperature, τ time, and $dt/d\tau$ are the corresponding cooling rates.

Subsequently, the method of regular heating and cooling was used by a number of authors to investigate the thermal conductivity of metals [3].

Our measuring apparatus was designed on the basis of the following considerations. By analyzing the solution of the problem for a spherical isotropic specimen, whose density, specific heat, and thermal conductivity do not depend on temperature, with a constant inward-directed heat flux at the surface it is possible to estimate the time starting from which the temperature field in the specimen may be assumed to be quasistationary. For this time the Fourier number

$$F = \frac{a\tau_0}{R^2} \geq 0.5 \quad (2)$$

The maximum temperature drop between the center of the sphere and its surface is

$$\Delta t = \frac{R^2}{6a} \frac{dt}{d\tau} \quad (3)$$

Here a is the thermal diffusivity and R the radius of the sphere.

The temperature averaged over volume (reference temperature) is

$$\langle t \rangle = t - \frac{R^2}{10a} \frac{dt}{d\tau} \quad (4)$$

where t is the temperature at the surface of the specimen.

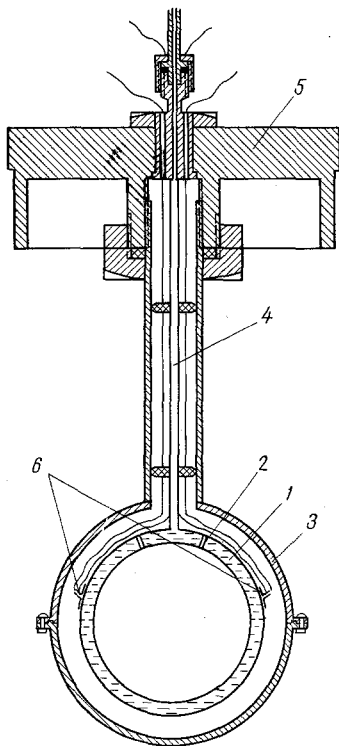


Fig. 1

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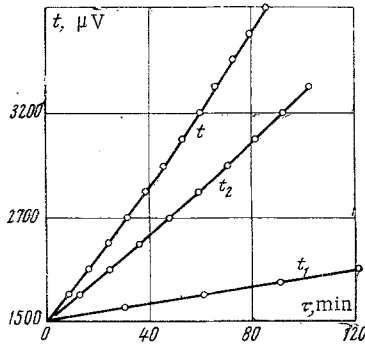


Fig. 2

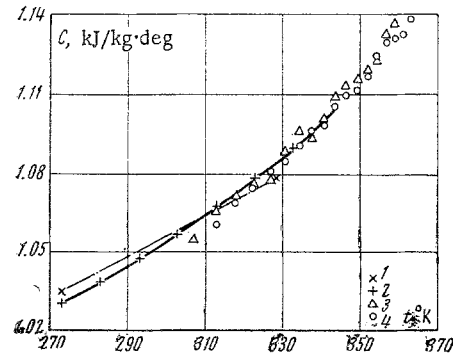


Fig. 3

Assigning a satisfactory heating rate of the order of 6–10 deg/h, we make the necessary estimates. For a sphere with a radius of 30 mm filled with water $\tau_0 \sim 0.9$ hr, $\Delta t \sim 1^\circ\text{C}$. The thermal diffusivity of Freons is 3–4 times less than that of water, and correspondingly we have $\tau_0 \sim 3$ hr, $\Delta t \sim 3.5^\circ\text{C}$.

Clearly, the results are unsatisfactory. Good results are obtained for a sphere with a radius of 10 mm. The time τ_0 is then reduced to 10–20 min, and the temperature drop Δt to tenths of a degree.

In this case, however, the relationship between the specific heats of the calorimeter and the liquid filling it sharply deteriorates.

Nonetheless, the same result for τ_0 and Δt is obtained if we consider not a liquid-filled sphere, but a spherical layer between two coaxial spherical shells. In this case it is even possible to reduce the thickness of the layer to 5 mm, while retaining a favorable relationship between the specific heats of the calorimeter and the test liquid.

The experimental calorimetric system is illustrated in Fig. 1. The inner 2 and outer 1 calorimeter shells are made of 1Kh18N8T stainless steel 0.3 mm thick, the corresponding diameters being 50 and 60 mm. The exterior shell 3 is made of copper 4 mm thick. The air gap is 10 mm wide. A stainless-steel capillary 4, 1 mm in diameter, connects the calorimeter with the filling system and a vacuum pump. A constant pressure is maintained by a thermocompressor. The entire calorimetric system is attached to the cover of the constant-temperature chamber 5.

The ends of chromel-alumel thermocouples 6, made of 0.3-mm wire, are attached to shell 1. These ends are inserted in thin sleeves ($\delta = 0.2$ mm) to ensure reliable contact with the surface of the sphere. One thermocouple forms part of a differential thermocouple, whose other end is imbedded in the exterior shell 3. The other thermocouple is used to measure the temperature at the calorimeter surface.

Estimates of the Biot number of the heat receiver in different regimes give values on the interval $B \sim 0.003$ – 0.03 . This makes it possible to measure the temperature of the exterior shell at one point.

The reference temperature is determined by introducing a correction in accordance with Eq. (4).

As a result of heating a temperature difference, which is subsequently kept constant, is created between the copper shell 3 and shell 2 of the calorimeter; a R-306 potentiometer is used for monitoring purposes, but at this stage regulation is manual, with a galvanometer serving as null detector.

Once the operator has acquired a certain skill, the zero drift does not exceed 0.05°C at a temperature difference of 6– 12°C .

The experiment consists in recording the heating curves of the empty calorimeter and the calorimeter filled with the calibration liquid (water) and the test liquid. The liquid is heated continuously up to the saturation line. The formula for the specific heat of the test liquid C_2 takes the form

$$C_2 = C_1 \frac{v_2 t' / t_2' - 1}{v_1 t' / t_1' - 1}, \quad C_2 = C_1 \frac{v_2 \tau_1' - \tau_2'}{v_1 \tau_1' - \tau_2'} \quad (5)$$

Here, C_1 is the specific heat of the calibration liquid, v_2 and v_1 are the specific volumes of the test and calibration liquids, t' is the empty calorimeter heating rate, t_1' and t_2' are the heating rates for the calorimeter filled with the calibration and test liquids, τ_1' are the reciprocals of the heating rates.

The experimental $t(\tau)$, $t_1(\tau)$, and $t_2(\tau)$ curves, recorded at a temperature difference between the calorimeter and the shell of the order of 6°C , are presented in Fig. 2. The time was measured correct to 0.2-0.3 sec with a stopwatch. The thermocouple emf was measured with the R-306 potentiometer as the galvanometer light spot passed through zero.

In view of the considerable difference between the heating rates of the empty and the liquid-filled calorimeter, the temperature measurements are affected by dynamic distortions. Their influence on the accuracy of determination of the specific heat is slight only at commensurable heating rates of the empty and liquid-filled calorimeters. A rough estimate of the constant of thermal inertia of the heat receivers makes it possible to establish an upper limit for the heating rate difference such as to ensure an accuracy of $\pm 5\%$ in determining the specific heat. This limit is roughly equal to 60-80 deg/h when suitable corrections are introduced.

However, it should be taken into account that as the specific heat of the calorimeter decreases there is a considerable reduction of the relative error that it introduces into the result, as follows from an analysis of the calculation formula.

The relative errors of the heating rates are calculated from the formulas

$$\delta t' = \frac{t_2' - t_1'}{(t' - t_1')(t' - t_2')} \Delta t', \quad \delta t_1' = \frac{t'}{t_1'(t' - t_1')} \Delta t_1', \quad \delta t_2' = \frac{t'}{t_2'(t' - t_2')} \Delta t_2' \quad (6)$$

In determining the reference temperature without introducing a correction, in accordance with Eq. (4) the maximum possible error is less than 0.1% in view of the weak temperature dependence. On the other hand, given two calibration liquids, it is generally possible to eliminate the specific heat of the calorimeter from the calculation formula. It then becomes unnecessary to record the heating curve of the empty calorimeter. In this case, we employ the formula

$$C_3 = \frac{v_3}{\tau_1' - \tau_2'} \left[\frac{C_1}{v_1} (\tau_3' - \tau_2') - \frac{C_2}{v_2} (\tau_3' - \tau_1') \right] \quad (7)$$

Here, τ'_i are the reciprocals of the heating rates; the subscripts 1 and 2 relate to the two calibration liquids, and the subscript 3 to the test liquid.

We used the apparatus described above to measure the specific heat of Freon 21 on the saturation line up to pressures of 11 bar. The measurements were made at two different temperature differences between the shell and the calorimeter: ~ 6 and 12°C . The heating rates were determined directly in $\mu\text{V}/\text{sec}$. Data on the density of Freon 21 on the saturation line were taken from [4]. The results of the measurements are presented in Fig. 3, where 3 represents the series of points obtained at a temperature drop $\sim 12^\circ\text{C}$, 4 those obtained at $\sim 6^\circ\text{C}$. The same figure also includes the experimental data obtained by Benning on the temperature interval from -12.1 to 55.2°C and by the Leningrad Technical Institute of the Refrigeration Industry (LTIKhp) on the interval from -64 to 59°C . The accuracy of the LTIKhp data is estimated by the authors at $\pm 1\%$.

As may be seen from Fig. 3, there is satisfactory agreement between our results and the earlier data. The maximum deviation in the region of overlap does not exceed 0.6%. After correlating the results we obtained an empirical expression for the specific heat (in $\text{kJ}/\text{kg}\cdot\text{deg}$) on the saturation line as a function of temperature ($^\circ\text{C}$):

$$G_p = 1.0342 + 3.449 \cdot 10^{-4} t + 9.578 \cdot 10^{-6} t^2 \quad (8)$$

for the temperature interval $34-90^\circ\text{C}$.

The maximum deviation from the curve was 0.7%, the mean-square error 0.28%.

The error of the results obtained, allowing for the calibration error and possible systematic errors, does not exceed $\pm 0.5\%$. The chief contribution to the error is introduced in differentiating the time dependence of the temperature during heating. It should be kept in mind, however, that these curves are quite smooth (the scatter does not exceed 0.01-0.02%) and very well reproducible. Thus, in four repeat measurements of the specific heat of Freon 21 we recorded the same $t_2(\tau)$ dependence. The maximum deviation of the heating time for a constant temperature difference of the order of 30°C was less than $\pm 0.05\%$ without corrections.

Thus, the method is characterized by the simplicity of the apparatus and the experimental technique, as well as by its speed and the accuracy of the results.

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