

USE OF THE REGULAR REGIME FOR THE INVESTIGATION  
OF THE THERMAL CONDUCTIVITY OF LIQUID FREONS

O. B. Tsvetkov

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A description is given of an experimental apparatus to determine the thermal conductivity of liquids and gases at various pressures and temperatures by the method of the regular regime. A formula for calculating the thermal conductivity from experimental measurements has been obtained.

The cylindrical bicalorimeter method has been used to determine the thermal conductivity of Freons 22, 113, and 142. Changes have been made in both the construction of the instrument and in the method of investigation compared with existing solutions [1].

Let us examine a system consisting of a metal cylinder covered with an insulating sheath, a thin layer of liquid or gas.

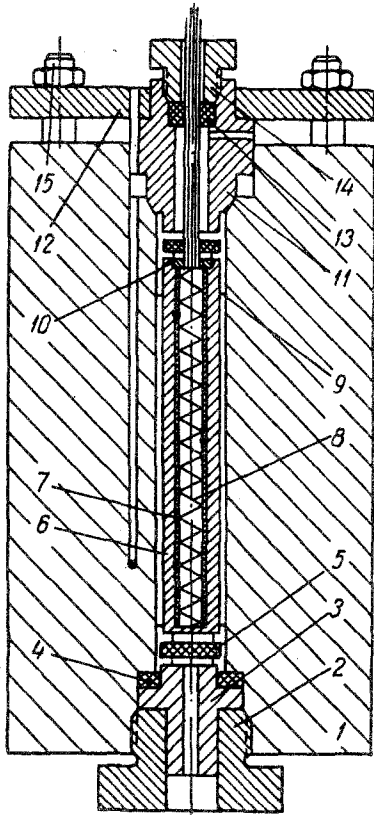


Fig. 1. Diagram of bicalorimeter: 1) Outer cylinder; 2) clamping nut; 3) packing cone; 4) gasket; 5) textolite cylinders; 6) inner cylinder, core of bicalorimeter; 7) copper tube 5 mm in diameter; 8) heater; 9) porcelain pins; 10) copper cover; 11) upper cone; 12) flange; 13) capillary; 14) clamping nut; 15) pins.

We make certain assumptions about the system: heat is transmitted in the layer only by thermal conduction; the outer surface of the layer is maintained at a constant temperature equal to that of the surrounding medium; the thickness of the layer surrounding the inner cylinder — the core of the bicalorimeter — is many times less than the least of the linear dimensions of the core; the cylinder is made of a material with high thermal conductivity and a specific heat much greater than that of the layer.

Proceeding from these assumptions, we shall examine the insulating sheath as a thin-walled plane layer. Then the temperature drop in the layer in the regular regime will be given by

$$\vartheta = \vartheta_{z=0} A_1 \sin \eta_1 \exp(-m \tau), \quad (1)$$

$$A_1 = 2\eta_1 \{ \eta_1^2 [1 + \sin^2 \eta_1 (2/\beta) - \sin 2\tilde{\eta}_1/2\eta_1] \}^{-1}, \quad (2)$$

$$m = a \eta_1^2 / \delta^2. \quad (3)$$

In (3)  $\eta_1$  is the first root of the equation

$$\operatorname{ctg} \eta_n = \eta_n / \beta, \quad (4)$$

which may be found from the condition  $\beta = C_0/C_c \ll 1$  by expanding  $\operatorname{tg} \eta$  in the series [2, 3]:

$$\eta_1 = \sqrt{\beta(1 - \beta/3)}. \quad (5)$$

Knowing  $\eta$ , we obtain from (3)

$$m = \frac{a}{\delta^2} \beta (1 - \beta/3) = \frac{\lambda F}{C_c \delta} (1 - \beta/3). \quad (6)$$

$$\lambda (m \delta / F) (C_c + C_0/3). \quad (7)$$

Of the total heat flux passing through the layer of material examined, a part travels by various thermal bridges other than the sheath. Consequently, the value of  $\lambda$  obtained from (7) exceeds the true value  $\lambda_0$  by an amount given by

$$\lambda - \lambda_0 = \left( \frac{2\lambda_e F_e}{\delta_e} \frac{\lambda_l}{\delta_l} F_l + \frac{\lambda_v}{\delta_v} F_v \right) \frac{\delta}{F}. \quad (8)$$

No great reliability can be claimed for this formula because of various assumptions about heat transmission through thermal bridges, because it is impossible to calculate heat losses resulting from any distortion of the temperature field at

the ends of the core, and because of other considerations. It is therefore preferable to determine the correction by a direct test with a substance whose thermal conductivity is low and well documented, for example, dry air.

Allowing for this correction, the conductivity of the sheath is finally given by

$$\lambda_0 = Am(1 + \beta/3) - B. \quad (9)$$

Under the conditions assumed, formula (9) can be recommended for all types of bicalorimeters.

A cylindrical bicalorimeter (Fig. 1), constructed according to the above assumptions, has been used to measure thermal conductivity.

The bicalorimeter consists of two coaxial cylinders with a layer of the investigated liquid in between.

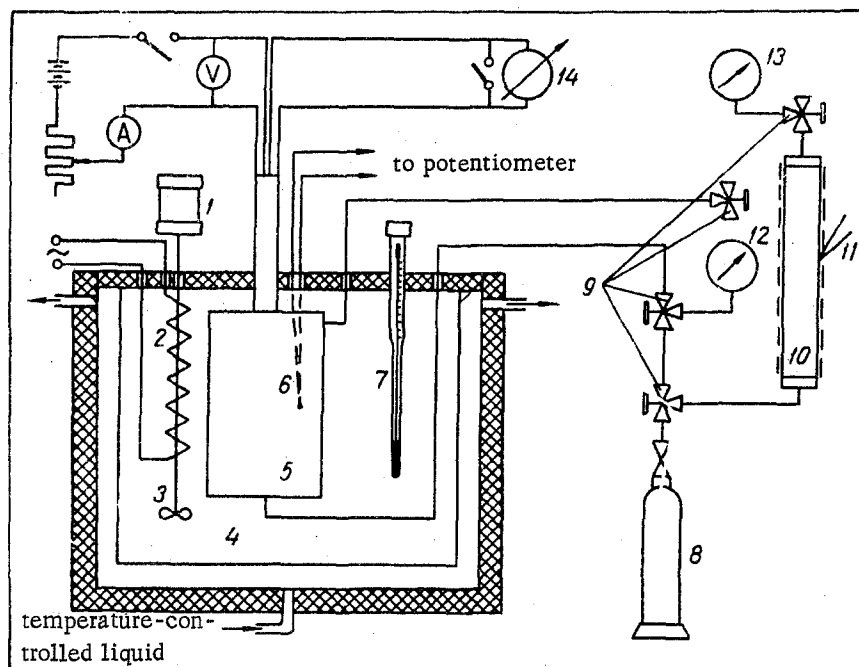


Fig. 2. Diagram of experimental setup: 1) electric motor; 2) heater; 3) stirrer; 4) temperature-regulated chamber 5) cylindrical bicalorimeter; 6) thermocouples; 7) Beckmann thermometer; 8) bottle of test liquid; 9) high-pressure valves; 10) thermal booster; 11) thermocouples; 12, 13) manometers; 14) mirror galvanometer.

The outer cylinder is a massive block of electrolytic copper (height 320 mm, diameter 108 mm, weight 23 kg), along the axis of which a hole 15.110 mm in diam. and 200 mm long is drilled. Inside the hole is a cylinder 13.570 mm in diam. and 130 mm long, the core of the bicalorimeter. The gap between the cylinders is held constant by 1-mm porcelain pins, three at each end of the inner cylinder. The coaxial surfaces of the cylinders were carefully polished and plated with nickel and chromium.

A special feature of the instrument is the copper inner cylinder, which contains a heater and three layers of differential thermocouples. A solid and reliable contact was achieved with a copper tube about 5 mm in diameter and 128 mm long, with three longitudinal channels for locating the thermocouple junctions (shown by points in Fig. 1).

For better thermal contact the junctions were welded to the wall of the copper tube. The site of the packing was carefully cleaned and ground. The copper tube, in the assembled condition, is pressed along the axis of the cylinder, and inside it is placed a heater of constantan wire insulated with silk and lacquer bifilar-wound onto a spiral copper frame of variable pitch.

The heater and the thermocouple junctions are insulated from the test liquid by a thin-walled stainless steel capillary and a thin copper cover, screwed to the top of the cylinder. The capillary was soldered to the copper cover with silver solder.

To simplify construction of the bicalorimeter, we dispensed with protective cylinders.

Besides the greater length of the inner cylinder in comparison with its diameter, the ends of the core were insulated with epoxy resin to reduce extraneous heat losses, and to exclude convection, the remaining space was filled with tex-

tolite cylinders.

The bicalorimeter was sealed with two cones, which served at the same time for filling, washing, and evacuating the instrument.

The inlet and outlet were formed by 3-mm copper tubes sweated into the body of the cones.

To house the cold junctions of the differential thermocouples, which were also insulated from the test substance, three holes 3 mm in diam. were drilled in the body of the outer cylinder, along a generator. The thickness of the wall thus formed between the site of a thermocouple junction and the surface of the central hole did not exceed 2 mm.

The experimental setup is shown in Fig. 2.

The bicalorimeter was suspended vertically in a 50-liter temperature-controlled chamber, equipped with a powerful motor-driven axial stirrer, a 1000 watt heater, and a cooler.

Inside both walls of the chamber liquid at a controlled temperature was circulated. This maintained a constant temperature correct to  $\pm 0.005^\circ\text{C}$  over a period of half an hour. A Beckmann thermometer gave a check on the constancy of the temperature.

For temperatures below  $0^\circ\text{C}$  a Dewar flask, filled with alcohol and cooled to the required temperature with dry ice, was used. The alcohol was stirred periodically. The uniformity of temperature distribution with height was checked with a bank of mercury and alcohol thermometers to a scale accuracy of  $0.1-0.2^\circ\text{C}$ .

Temperature control was achieved from the readings of a copper-constantan thermocouple embedded in the body of the bicalorimeter; the readings were led out to a potentiometer with a galvanometer.

The pressure in the equipment was increased by heating the liquid in a thermal booster. The heating was controlled by a manual system of rheostats and an autotransformer.

The pressures in the bicalorimeter and the booster were measured with a spring manometer.

When the required pressure was attained in the bicalorimeter, the booster was disconnected, and the apparatus closed off by the appropriate valve.

To measure temperature difference and to increase the sensitivity, a six-junction differential thermocouple was used. Copper and constantan 0.1 mm in diameter with silk and lacquer insulation were used as electrodes. The junctions were formed by soldering.

Since the measured temperature differences were usually small, a mirror galvanometer was used to determine the thermocouple emf.

The bicalorimeter heater was fed from six batteries; the current and voltage were controlled by an ammeter and voltmeter.

Time readings in the experiments were made with three stopwatches with 30- or 60-second scales, depending on the rate of cooling.

A number of preparatory steps preceded the tests.

The first of these was careful measurement of the diameters of the central hole and the inner cylinder of the bicalorimeter and accurate weighing, and a check on the axial alignment of the cylinders by means of a glass capillary of appropriate size. The value of the gap obtained as a result of these measurements was  $\delta = 0.77 \pm 0.01$  mm.

From these data the bicalorimeter constant A and the heat capacities  $C_C$  and  $C_0$  were calculated.

The next operation was filling the bicalorimeter, for which purpose the instrument was carefully evacuated and purged with vapor of the test liquid.

Good repeatability at values of  $\lambda_0$  to 0.5-1.0% for three different fillings indicated absence of air bubbles in the liquid. In all of the tests the core was heated for 3-9 min, and the measured temperature difference in the layer was  $1.5-0.4^\circ\text{C}$ , depending on the physical properties of the liquid and the test temperature.

Before each series of measurements, the region of regularization was determined by drawing the graph  $\ln n - \tau$ . In this region three sections were selected, in which the rate of cooling was also measured. This allowed a simultaneous check on the regularization process and on the absence of convection in the layer.

The thermal conductivity of the liquid was calculated from formula (9).

The correction B was determined experimentally. For this purpose tests were run with air previously dried and purified in concentrated sulfuric acid and a calcium chloride filter.

The thermal conductivity of dry air at 20°C was assumed to be  $\lambda_0 = 0.0256$  watt/m.deg.

The tests showed that the value of B remained constant in the whole range of temperature investigated. Then the equation of the bicalorimeter for 20°C takes the form

$$\lambda_0 = 8.48m \left( 1 + \frac{1}{3} \beta \right) - 0.0049. \quad (10)$$

The values  $C_C$  and  $C_0$  vary with temperature, and this is allowed for with the aid of special graphs.

Toluene was taken as a standard for checking the equipment; its thermal conductivity, measured at atmospheric pressure and temperatures from -80 to +90°C, showed good agreement with published data [4].

Measurements were made of the conductivity of Freon 22 (-80 to +70°C), Freon 113 (-20 to +90°C), and Freon 142 (-80 to +90°C) in the liquid phase at the saturation line (see table).

Thermal Conductivity of Freons

t, °C	-80	-60	-40	-20	0	20	40	60	70	90
Substance	$\lambda$ , watt/m • degree									
Freon 22	0.138	0.128	0.118	0.108	0.0977	0.0875	0.0770	0.0646	0.0565	—
Freon 142	0.126 <sub>4</sub>	0.118 <sub>4</sub>	0.110 <sub>6</sub>	0.102 <sub>7</sub>	0.0948	0.0869	0.0790	0.0711	0.0672	0.0564
Freon 113	—	—	—	0.868	0.822	0.777	0.731	0.686	0.664	0.619

In our tests the product of the parameters GrPr does not exceed the allowable value, and therefore the effects of free convection on the results of the experiments were not taken into account.

In no case did the scatter of the experimental points about the average curve exceed  $\pm 1.0$  to  $\pm 1.5\%$ .

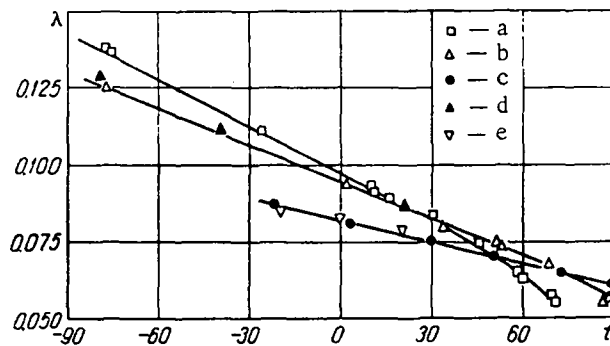


Fig. 3. Thermal conductivity of liquid Freons: a, b, and c) Present results for Freons 22, 142, and 113; d and e) experiments on Freon 22 [5] and on Freon 113 [6].

As may be seen from Fig. 3, our data on Freon 22 show good agreement with the results of [5] and [6] at 20°C. In the negative temperature region our results are higher than the data of [5] by 7% at -80°C.

Data on the thermal conductivity of Freon 22 at temperatures above +20°C and data giving the dependence of the conductivity of Freon 142 on temperature were obtained for the first time.

The results of our investigations show good agreement with the measurements of [6] for Freon 113.

#### NOTATION

$\lambda$  - thermal conductivity;  $m$  - cooling rate;  $C_C$  - total heat capacity of the core;  $C_0$  - heat capacity of the layer of test liquid;  $\delta$  - thickness of liquid layer;  $\vartheta$  - temperature difference;  $a$  - thermal diffusivity;  $F$  - calculated surface area of layer  $A = C_C \delta / F$  - constant of bicalorimeter;  $B$  - correction for heat losses;  $t$  - temperature. Subscripts: "0," "e," "l," and "v" relate, respectively, to the liquid layer, the ends of the cylinder, the thermocouple and heater leads, and the capillary.

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Institute of Industrial Refrigeration Technology,  
Leningrad