INVESTIGATION OF THERMAL CONDUCTIVITY OF LIQUID FREONS

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The temperature dependence of the thermal conductivity of five liquid freons is experimentally investigated. An empirical relation for generalization of the obtained data is offered. The thermal conductivity of liquid Freons 11, 21, 114, and 115 is calculated.

In thermo-physics the thermal conductivity of liquid freons is one of the most important constants. Its experimental study, expecially over a wide range of temperatures, presents great difficulties. For this reason it is of especial interest for heat computations to obtain data on thermal conductivity by calculation.

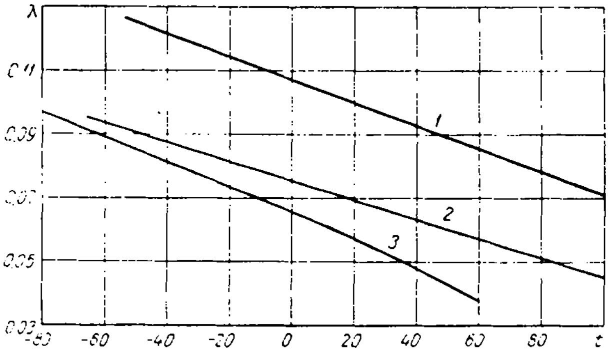

Fig. 1. Computed values of thermal conductivity of liquid freons: 1) Freon 21; 2) Freon 114; 3) Freon 115.

To solve this problem it is necessary to have quite reliable and well-substantiated experimental data, since there are considerable divergencies between the results of the experimental investigations of various authors. In this connection we made measurements of the thermal conductivity and its dependence on temperature for liquid Freons 12(CF_2Cl_2), 13(CF_3Cl), 22(CHF_2Cl), 113($C_2F_3Cl_3$) and 142($C_2H_3F_2Cl$). At the present time these substances are widely used in refrigeration, chemistry, instrument making, medicine, and other branches of the national economy. Of particular interest is the use of data on the thermal conductivity of these substances in the design of heat-exchange apparatus in power installations which utilize the heat of geothermal sources.

The experiments were conducted in an apparatus based on the cylindrical bicalorimeter principle. The measuring apparatus was made of two coaxial copper cylinders, between which there was a 0.77 mm thick layer of test liquid. To measure the temperature differences within the liquid layer and to generate the heat flux, we used a triple-junction thermocouple and a heater along the axis of the inner cylinder. The thermocouple junctions located in the inner cylinder of the bicalorimeter and the heater were completely isolated from the test substance by means of a thin-walled capillary.

The design of the bicalorimeter included provision for pressurizing, loading, and evacuating the test space.

The ends of the inner cylinder were isolated with a layer of epoxy resin to reduce stray heat fluxes. Heat release at the cylinder ends was determined in tests with dry air.

The inner cylinder was centered along the axis of the outer cylinder by six porcelain brads; the centering was checked by a specially selected capillary of appropriate size.

The heater was powered by six storage batteries; a M17/1 mirror galvanometer was used to measure the cooling rate.

The bicalorimeter was placed in a liquid thermostat where an appropriate positive or negative temperature was maintained. After the device was loaded and pressurized, the heater was switched on and the inner cylinder slowly heated up.

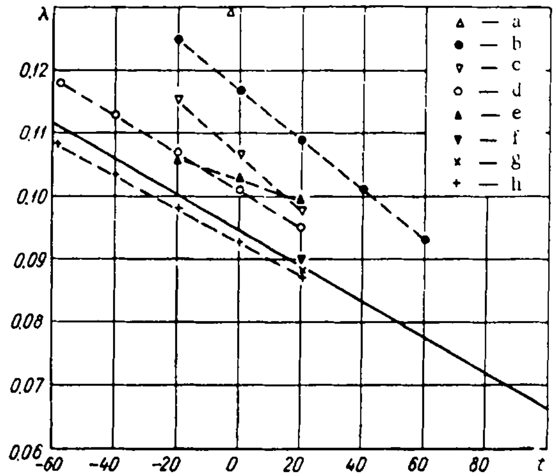

Fig. 2. Thermal conductivity of Freon 11: a) according to data of Malhotra [15]; b) Markwood and Benning [15]; c) Danilova [15]; d) Cherneeva [15]; e) Powell and Challoner [15]; f) Riedel [15]; g) Plank [15]; h) Widmer [16]; continuous line is in accordance with equation (2).

The experiment consisted of plotting the cooling curve, calculating the cooling rate and finally determining the thermal conductivity from the formula

$$\lambda = \frac{mC_c}{2\pi L_c} \ln \frac{D_2}{D_1} \left(1 + \frac{C_0}{3C_c} \right) - M. \qquad (1)$$

The experimental apparatus was checked with toluene. The data obtained in the temperature range −80° to +90° C (Table 1) are in good agreement with the most reliable values [1, 2].

In all the experiments the quantities Gr · Pr did not exceed the permissible values. Tests at different temperature drops in the layer showed that λ does not depend on Δt, this being one more confirmation of the absence of convection. The accuracy of the results of measuring the thermal conductivity is estimated at ±1.5%.

Based on a generalization of the obtained experimental material, it was established that the temperature dependence of thermal conductivity for all the investigated freons may be represented as follows:

$$\lambda = B\rho^n. \tag{2}$$

In contrast to the well-known Predvoditelev-Vargaftik equation [1], which, when applied to the given case, gives a considerable deviation from the experimental data, on the average +37%, relation (2) gives the thermal conductivity as a function of ρ^n.

The average values of the coefficient B calculated from the formula

$$B = \lambda/\rho^n, \tag{3}$$

are as follows: for Freons 12, 13, 22, 113, and 142, $B \cdot 10^4 = 4.197$, 4.297, 5.997, 3.141, and 6.966, respectively; the maximum deviations $\pm\Delta B = 1.38$, 1.33, 1.35, 0.41, and 0.79%. The value of n, taken to be equal to 2.00 for all freons, was found using coordinates log ρ and log λ. The density of liquid freons was determined on the basis of experimental data [3–5]. In equations (2) and (3) λ is given in W/cm·deg and ρ in g/cm^3.

Equation (2) was additionally checked by generalization of experimental data on the thermal conductivity of water, methane, ethane, oxygen, n-propane, and ammonia in the liquid phase obtained by various investigators.

Values of the coefficient B for the indicated liquids for λ in W/m · °C and ρ in kg/m^3 are presented in Table 2.

The effect of association of water was taken into account in the coefficient α using the data of [1].

The results of a generalization for 11 liquids makes it possible to state the following conclusions:

1. Coefficient B in (2) is practically independent of temperature. For a given liquid its value remains constant within the accuracy limits of the experiment.

2. Equation (2) gives the change in thermal conductivity on the saturation line within wide limits of temperature, including the critical. Thus, up to the critical temperature the results of λ measurements are described for n-propane [6] and for water [9]. The thermal conductivity of oxygen and ammonia is generalized by equation (2) up to $\tau = 0.95$ to 0.97.

Of practical interest is the possibility of computation of the thermal conductivity of freons from their chemical formulas. The need of such a method is evident from the considerable number of new chemical compounds, particularly freons, the rapid development of which considerably outstrips the possibilities of experimental determination of λ. Besides, not every new substance is promising and merits special study, and, in this sense, the indicated computation method is especially necessary.

Table 1

Thermal Conductivity of Liquid Freons

t, °C	λ, W/m·deg for freons				
	12	13	22	113	142
−80	0.1116	0.0984	0.1385	—	0.1264
−60	0.1039	0.0882	0.1283	—	0.1185
−40	0.0962	0.0780	0.1181	—	0.1106
−20	0.0885	0.0678	0.1079	0.0867	0.1027
0	0.0808	0.0545	0.0977	0.0822	0.0948
20	0.0731	—	0.0875	0.0777	0.0869
40	0.0654	—	0.0773	0.0732	0.0790
60	0.0577	—	0.0646	0.0687	0.0711
70	0.0530	—	0.0545	0.0664	0.0668
90	0.0418	—		0.0619	0.0561

Let us represent the coefficient B in (2) by analogy with the Predvoditelev-Vargaftik equation [1] in the form

$$B = Ac_p n^{-1}\mu^{-1/3}. \tag{4}$$

In this formula the values of A and c_p are referred to the same reduced temperature $\tau = 0.65$ which for all freons is close to the normal boiling point, where data on the c_p of liquids are very precise.

The values of constant A obtained for five freons from the formula

$$A = Bn\mu^{1/3}c_p^{-1} \tag{5}$$

are as follows: for Freons 12, 13, 22, 113, and 142, $A \cdot 10^3 = 4.592$, 4.706, 4.787, 3.680, and 5.223, respectively; $c_p = 0.904$, 0.858, 1.107, 0.975, and 1.239 J/g · deg at $\tau = 0.65$. The specific heat of freons at $\tau = 0.65$ was taken in accordance with the experimental data of [10–12].

An analysis of these data shows that constant A in (5) is not fixed for all the liquids, but depends on the structure of the freon molecule. The latter is composed of atoms. Thus, if we ascribe to the individual atoms definite values of the constant A, the molecular constant will be equal to the sum of the atomic constants

$$A = \sum_{1}^{n} A_R. \tag{6}$$

For carbon, chlorine, and fluorine atoms $A_R \cdot 10^3 = -6.41$, 2.75, and 2.75, respectively; for hydrogen $A_R \cdot 10^3 = 2.95$ at $q = 1$ and 3.26 at $q = 3$. In the calculation of the atomic constants from the above-cited data, values of A were taken into account for Freons 22, 113, and 142; and the value of the molecular constant for Freon 12, inasmuch as the available data on c_p for Freon 12 are more precise [10] than for Freon 13.

Table 2

Generalization of Experimental Data Using Equation (2)

Substance	Temperature, °C	B	$\pm\Delta B$, %	n	Reference
Water	0 to 340	$5.369\cdot10^{-4}$	1.1 (−8.2 at °C)	1.05	[6]
Methane	−173 to −103	$7.257\cdot10^{-7}$	0.4	2.06	[6, 8]
Ethane	−173 to −2	$5.862\cdot10^{-7}$	1.4	2.00	[6]
Oxygen	−200 to −130	$3.245\cdot10^{-7}$	0.7	1.85	[6, 7]
Ammonia	+ 20 to +120	$2.588\cdot10^{-5}$	1.1	1.53	[6]
n-Propane	+40 to +96.8 (crit)	$3.687\cdot10^{-3}$	1.0	0.50	[6]

The proposed method was used to compute the thermal conductivity of Freons 11($CFCl_3$), 21($CHFCl_2$), 114($C_2F_4Cl_2$), and a new and exceptionally promising liquid, Freon 115(C_2F_5Cl).

We will illustrate the calculation of the constant A and coefficient B on the example of Freons 115 and 11.

According to the chemical formula for Freon 115(C_2F_5Cl) and equation (6)

$$A = \sum A_R = x\cdot A_C + y\cdot A_F + z\cdot A_{Cl} + q\cdot A_H = 2\cdot(-6.41) + (1+5)\cdot 2.75 = 3.68\cdot 10^{-3},$$

for Freon 11($CFCl_3$)

$$A = -6.41 + (1+3)\cdot 2.75 = 4.59\cdot 10^{-3}.$$

According to (4) we have, respectively: for Freon 115

$$B = 3.32\cdot 10^{-4},$$

and for Freon 11

$$B = 4.00\cdot 10^{-4}.$$

The value of n was taken as equal to 2.00. The heat capacity at $\tau = 0.65$ was found from data taken from [10, 11, 13]. The density of Freon 11 was obtained from the data of [11]; the density of Freon 115 and partially of Freon 114 was calculated by the method of thermodynamic similarity [13], using Bubushyan's data as a standard, from the density of Freon 113 [14]; the density of Freon 21 and partially of Freon 114 was obtained from data in [3, 10].

The thermal conductivity of Freon 21 and Freon 114 was partially investigated, albeit within a small range of temperature (−20° to +20° C). The thermal conductivity of Freon 115 has not yet been investigated.

Since the greatest amount of experimental data relates to the thermal conductivity of Freon 11, this substance was selected as a standard for checking the reliability of the computed values (Fig. 1).

The results of computing the thermal conductivity of Freon 11, as may be seen from Fig. 2, do not confirm the experimental data of Malhotra, Markwood, and Benning and partially of Danilova.

The data of Riedel, Plank, and Widmer are in good agreement with our data. The divergence from the data of Cherneeva, Powell, and Challoner amounts to no more than 5–7%.

Satisfactory agreement between the obtained data and the most reliable experimental results indicates the reliability of the computed values of the thermal conductivity of the above-indicated freons.

The above-cited values of the atomic constants were obtained for freons which are derivatives of a homologous series of methane hydrocarbons, having in the molecules only single valence bonds between adjacent carbon atoms. Thus, double and triple bonds, and special locations of the individual atoms and groups in the molecule, require the introduction of supplementary bond increments and corrections.

NOTATIONS

λ—thermal conductivity; C_c and C_0—total heat capacities of inner cylinder and layer of test liquid; D_2 and D_1—outside diameter of layer and inner cylinder, respectively; m—cooling rate; M—correction for system heat loss; B—constant coefficient for given liquid; n—exponent; A—molecular constant of liquid; A_R—atomic constant; x, y, z, q—number of atoms of carbon, fluorine, chlorine, and hydrogen in the freon molecule; ρ—density of liquid; μ—molecular mass.

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