THERMAL CONDUCTIVITY OF FREON-12

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The construction of a heated filament measurement device is described. The thermal conductivity of Freon-12 in the liquid phase is measured over the temperature range –50-100°C at pressures up to $600 \cdot 10^5$ N/m^2, and conductivity of the gaseous phase of Freon-12 is measured over the range 30-160°C at atmospheric pressure. The results obtained are approximated by equations and compared with the data of other authors.

Freon-12 is widely used in industry for measurements of various technological processes and devices. It is thus necessary to know its coefficient of thermal conductivity (λ) over a wide range of state parameters. It should be noted that available data on λ of the liquid phase of Freon-12 are quite limited and contradictory (divergences as high as 15-20% in both absolute value of conductivity, and in its temperature derivative).

An experimental study has been made of λ in the liquid phase of Freon-12 over the temperature range –50-100°C at pressures up to $600 \cdot 10^5$ N/m^2, and in the gas phase over the range 30-160°C at atmospheric pressure. A modern variant of the measurement cell [1] using the absolute stationary heated filament method was used.

A schematic of the measurement device is shown in Fig. 1. Thin walled platinum and nickel capillaries were used as external resistance thermometers, thus eliminating the significant errors present in the classic variant of the heated filament method because of inaccuracies in measurement of the temperature drop across the glass capillary wall and uncertainty in referencing the temperature measured by the external resistance thermometer wound on the glass capillary.

The internal diameter and linearity of the metal capillaries were determined by a technique described in [1] to an accuracy of $\pm 3\,\mu$. A platinum filament 0.1 mm in diameter, serving as both the heater and the internal resistance thermometer, was threaded through the capillary. Potential leads to filament and capillary were prepared of platinum wire 0.04 mm in diameter. For insulation, the metal measurement capillaries were mounted in thick wall glass tubes, mounted with a radial gap of 0.3-0.4 mm in a large brass body. Centering of the capillary relative to the filament was accomplished through observation windows in the body walls with a UIM-21 microscope in two mutually perpendicular planes, using specially installed centering screws. The geometric characteristics of the measurement device are presented in Table 1.

The absence of significant radial gaps between walls of measurement capillaries, body, and autoclave permitted elimination of convective currents outside the working gap, which is especially significant in working with such low boiling point liquids as Freon, and also near the critical region.

Resistance thermometer calibration was done with two reference points (triple point and boiling point of water), and also with a specimen platinum resistance thermometer PTS-10, prepared and calibrated at VNIIFTRI every 20 degrees over the range –80-160°C.

The measurement device was installed in a stainless steel autoclave, mounted within a large copper block. To create isothermal conditions over the length of the device the copper block was located beneath a layer of thermostatic liquid with a low inertia thermostat and sensitive electronic temperature regulator,

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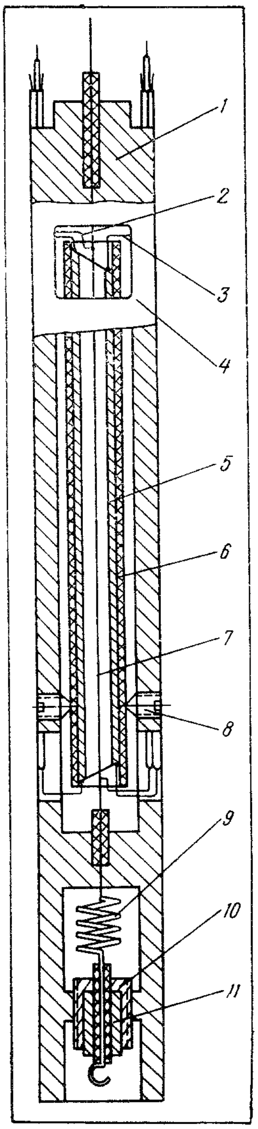


Fig. 1. Schematic diagram of measurement device: 1, 6, 11) glass capillaries; 2, 3) potential leads; 4) body; 5) measurement capillary; 7) platinum filament; 8) centering screws; 9) spring; 10) screw for filament tension adjustment.

ensuring no measurable temperature fluctuations within the autoclave. Pressure was generated and measured by a type MP-600, class 0.05 manometer. All voltage measurements were made with semiautomatic dc potentiometers type P-348, class 0.002 and P-309, class 0.005.

To allow for the effect of pressure and spring tension on resistance thermometer indication the internal thermometer was calibrated against the external before every experiment. Over the entire temperature and pressure range studied the correction to initial temperature did not exceed 0.01°C. To verify the absence of convection experiments were performed with 2-3 different values of temperature drop in the layer (from 2.5 to 6°C) and values of the complex GrPr < 1500. In calculating λ corrections were introduced for filament eccentricity, loss of heat from the ends, and changes in the measurement cell geometry, which did not exceed 0.3% in total. Due to the absence of IR absorption spectra of the liquid Freon-12 no correction for heat transfer by radiation was made, while for gaseous Freon this correction did not exceed 0.7%. The values of thermal conductivity obtained were referred to the arithmetic mean temperature of the layer. Analysis of the errors involved in the method indicates that the maximum relative error in the experimental data does not exceed ±1.2%.

In control experiments the thermal conductivity of toluol was measured over the temperature interval 0-160°C at pressures up to $600 \cdot 10^5$ N/m^2. Also used was nitrogen at atmospheric pressure over the range 40-160°C. The λ-values obtained for toluol agreed within 0.5% with those published earlier in [3], as well as those recommended in [4].

The Freon-12 used in the experiments was synthesized at the State Institute for Applied Chemistry. Purity analysis performed with KhL-69 and KhT-8 chromatographs indicated that the basic component

TABLE 1. Geometric Characteristics of Measurement Devices

Platinum filament diameter, mm	Length of working section, mm	Measurement capillary material	Internal diameter of capillary, mm	External diameter of capillary, mm	Mean eccentricity, mm
0,100	81,471	Platinum	1,100	1,200	0,012
0,100	87,170	"	1,398	1,600	0,015
0,100	89,192	"	1,900	2,002	0,022
0,100	81,460	Nickel	0,900	1,000	0,012
0,100	105,070	"	1,450	1,550	0,018

TABLE 2. Smoothed Values of Thermal Conductivity of Liquid Freon-12 ($\lambda \cdot 10^4$, W/m·deg)

Temperature, °C	Pressure, $p \cdot 10^{-5}$, N/m²				
	50	100	200	400	600
—50	952	976	1019	1089	1139
—40	916	940	984	1056	1107
—30	881	906	951	1024	1077
—20	847	872	918	994	1049
—10	814	840	887	964	1022
0	782	808	857	937	996
20	722	749	800	885	949
40	665	694	747	838	908
60	612	643	699	796	872
80	564	596	656	760	842
100	519	553	617	728	818

comprised 99.9%, satisfying government standard GOST 8501-57. Experiments were performed in measurement cells with gaps of 0.4 and 0.5 mm on isotherms at 20-30°C steps at pressures of 50.0, 197.1, 393.2, and $589.4 \cdot 10^5$ N/m². More than 50 experimental values for λ of liquid Freon-12 were obtained over the temperature and pressure range studied. The experimental data are presented in Fig. 2, with smoothed values after adjustment in $\lambda - p$ and $\lambda - t$ sections in Table 2.

To approximate the thermal conductivity values obtained, a form of equation was chosen which relates λ directly to the measured parameters temperature and pressure. As a result of processing by the method of least squares on an electronic computer the expression

$$\lambda \cdot 10^4 = 754{,}9 - 3{,}196\,t + 0{,}0049\,t^2 + (5{,}615 \cdot 10^{-6} + 1{,}167 \cdot 10^{-8}\,t + 3{,}750 \cdot 10^{-11}\,t^2)\,p - 2{,}661 \cdot 10^{-14} p^2, \tag{1}$$

was obtained, describing the experimental data with a maximum error of 0.6% and mean square error of 0.2%.

Table 3 shows values of λ calculated by Eq. (1) on the saturation line. Corresponding saturation pressures were taken from [5].

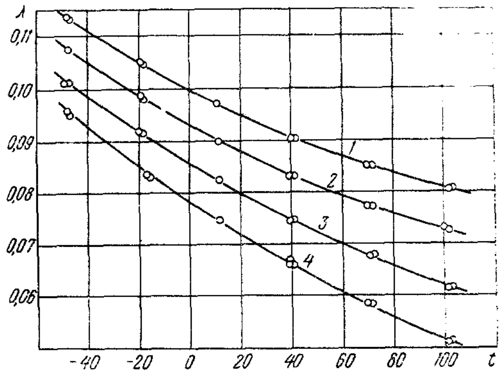
A comparison of the experimental λ-values of liquid Freon-12 on the saturation line with the data of various authors is presented in Table 4. Analysis of the data presented indicates that the results of studies [13, 14] using the heated filament method, as well as Riedel's data [7], using two independent methods, agree quite well with the values of λ measured here. The data of Markwood and Benning [8] and Danilova [9] show significantly higher values (15-30%), evidently connected with the presence of convective heat transfer in their measurements.

The results of [15], extrapolated along the saturation line, lie 4-7% higher than our results, while at a pressure of $5 \cdot 10^5$ N/m² they are 3-4% high. Unfortunately, the absence of a detailed description of the experimental apparatus and methodology in [15] did not allow an analysis of the causes of this divergence.

It should be noted that the thermal conductivity of Freon-12 at pressures up to $250 \cdot 10^5$ N/m² was calculated in the studies of Tsvetkov [16, 17], with λ of Freon-12 in the saturated liquid state taken from

TABLE 3. Thermal Conductivity of Freon-12 on Saturation Line

t, °C	—80	—60	—40	—20	0	20	40	60	80	100
$\lambda \cdot 10^4$, W/m·deg	1042	964	891	821	757	696	641	591	546	508



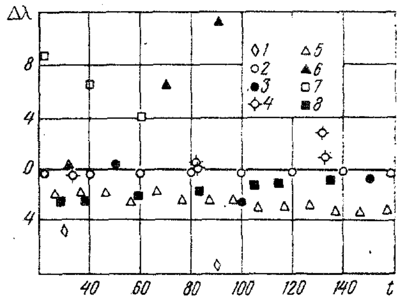


Fig. 2 Fig. 3

Fig. 2. Experimental values of coefficient of thermal conductivity (W / m · deg) of liquid Freon-12: 1) at 589.4; 2) 393.3; 3) 197.1; 4) $50.0 \cdot 10^5$ N / m^2. λ, W / m · deg; t, °C.

Fig. 3. Deviation (%) of data of various authors from values of thermal conductivity of gaseous Freon-12 measured in present study: 1) [8]; 2) [17]; 3) [18]; 4) [19]; 5) [20]; 6) [14]; 7) [10]; 8) [21]. t, °C.

the results of [12] and pressure considered by means of experimental data on λ of liquid oxygen, processed in the form of the dependence of corrected thermal conductivity on corrected temperature and pressure. Comparison of our λ-values with the results of [16, 17] shows that the disagreement at $5 \cdot 10^5$ N / m^2 reaches significant values, and $\partial\lambda / \partial p$ along the isotherms proves to be increased by a factor of 3-4 times.

Thus the method of data processing used in those experiments, possibly valid for thermodynamically similar substances, is of little application in calculating λ of Freon-12 under pressure.

For gaseous Freon-12 more than 30 experimental values of λ were obtained in the temperature range 30-160°C under atmospheric pressure. The results were approximated by the equation

$$\lambda \cdot 10^4 = 86.3 - 0.502\,t, \tag{2}$$

which describes the experimental data with a maximum error of 0.5% and mean square error of 0.2%. Figure 3 shows the deviation of data of various authors from the λ-values obtained here for gaseous Freon. The results of Tsvetkov [17], Keyes [18], Sherratt – Griffiths [19], Masia [21], and Gruzdev – Shestova – Selin [20] at p = 1.5 bar differ from our data by no more than 2-3.5%. The discrepancies with the results of [8, 10], lying beyond the limits of experimental error, are 6-8%, while divergence with [14] is 12%. Thus

TABLE 4. Comparison of Experimental Data on Thermal Conductivity of Freon-12

Authors	Source	Method	Temperature interval, °C	Pressure, N/m^2	$\lambda_{20} \cdot 10^4$, W/m · deg	$\partial\lambda/\partial t \cdot 10^4$, W/m · deg
Griffiths, Awbery, Powell	[6]	p	5—20	saturation pressure	645	5,2
Riedel	[7]	p.c	20	"	720	—
Markwood, Benning	[8]	f	0—75	"	890	6,0
Danilova	[9]	r	—30—0	"	826*	6,8
Cherneeva	[10]	f	—55—20	"	720	4,7
Powell, Challoner	[11]	p	—20—20	"	750	3,0
Tsvetkov	[12]	r	—80—90	"	731	3,9
Djalalian	[13]	f	—57—20	"	720	2,9
Sadykov, Gabdrakhmanov, Brykov, Mukhamedzyanov	[14]	f	—150 to—40	"	—	3,8
Gruzdev, Shestova, Shumskaya	[15]	c	30—200	$10—55 \cdot 10^5$	670*	2,8
Present study	—	f	—50—100	$50—600 \cdot 10^5$	696*	2,8

Note. p) plane layer method; c) coaxial cylinders; f) heated filament; r) regular thermal regime method.

*Extrapolated values.

the data on λ for gaseous Freon-12 agree with each other better than for the liquid state, a fact evidently connected with the decrease in experimental difficulties in measurement of thermal conductivity of gases.

It should be noted that the experimental data on thermal conductivity of liquid Freon-12 at high pressures have been obtained here for the first time.

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