THERMAL CONDUCTIVITY OF FREONS F-13V1 AND F-23 OVER A WIDE RANGE OF STATE PARAMETERS

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An experimental study of thermal conductivity of Freons F-13V1 and F-23 is presented. Equations are presented describing the thermal conductivity of Freon F-13V1 in the liquid phase and on the saturation line.

The development of low-temperature and cryogenic technology requires a knowledge of the thermophysical properties of cooling-apparatus working media over a wide range of state parameters, including the region near the crystallization temperature. The study of thermophysical properties at low temperatures is of special significance for the development of the theory of the liquid state, inasmuch as such data may be used to obtain valuable information on liquid structure.

For the above reasons the authors have performed an experimental study of the behavior of the coefficient of thermal conductivity λ of Freon F-13V1 over the temperature range –168 to +160°C and of Freon F-23 over the range –155 to 0°C at pressures to $600 \cdot 10^5$ Pa. Measurements were performed by the static heated-filament method. A thin-walled platinum capillary was used as the measurement-cell reference resistance thermometer, which increased the accuracy of the thermal-conductivity coefficient measurements [1]. A description of the experimental apparatus and technique of λ determination at moderate and high temperatures is presented in [2].

A sketch of the low-temperature apparatus is presented in Fig. 1. The basis of the apparatus is a cryostat consisting of a copper body with a bifilar wound coil of copper tubing 3 mm in diameter. To improve heat-transfer conditions the coil was tinned. To reduce spurious heat transfer the system was isolated within a high-vacuum casing inside which a heat shield screen was installed.

To maintain the required temperature, liquid nitrogen was supplied to the coil and exhausted by a vacuum pump through a differential needle valve, which allowed very accurate adjustment of the nitrogen flow rate. Some overcooling was compensated for by the thermal flux of electrical control heaters switched into the circuit by a sensitive position-type electrical thermostat. The temperature sensor used was a 100-Ω platinum resistance thermometer installed in a drilling in the copper block and series connected to a 20-Ω copper thermometer, bifilar wound on the block surface. Temperature field inhomogeneity over the length of the autoclave was monitored by copper–Constantan thermocouples, and absolute temperature measurement was performed by a reference 100-Ω platinum resistance thermometer, type TSPN-2A, prepared and calibrated at the All-Union Scientific-Research Institute of Physicotechnical and Radiotechnical Measurements.

Testing of the experimental apparatus at low (to –190°C) temperatures showed that the thermostat system used allowed very reliable maintenance of the autoclave temperature at a given level with deviations no greater than ±0.02 deg. The temperature gradient over the length of the measurement cell did not exceed $2 \cdot 10^{-4}$ deg/mm.

Experimental pressure was generated and measured by a piston load manometer type MP-600, class 0.05. Separation of the hydraulic press oil and the substances studied was accomplished by a U-shaped high-pressure mercury vessel.

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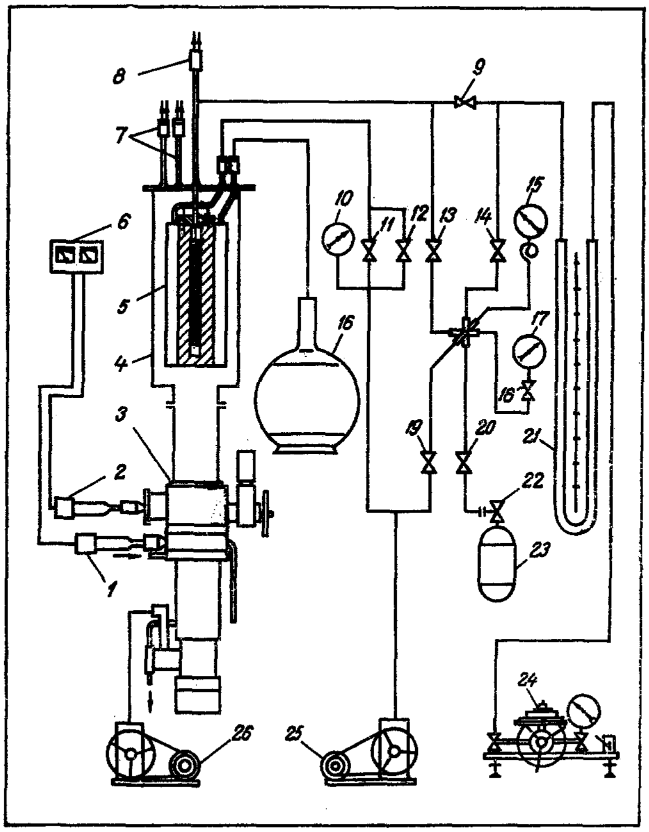

Fig. 1. Diagram of experimental apparatus: 1, 2) vacuum sensors; 3) vacuum apparatus; 4) casing; 5) cryostat unit; 6) vacuum meter; 7, 8) electrical inputs; 9, 11, 12, 13, 14, 18, 19, 20, 22) valves; 10, 17) vacuum meters; 15) manometer; 16) Dewar flask; 21) separation vessel; 23) container; 24) piston load manometer; 25, 26) vacuum pumps.

Measurement-cell thermometer resistance was determined by the compensation method using constant-current potentiometers type R-348, class 0.002, and type R-309, class 0.005. To eliminate the effect of parasitic thermo-emf the thermometer circuits were reversed by thermocurrentless switches, type P-308.

Proper operation was verified in control experiments with a reference medium, toluol, in the temperature interval −95 to 0°C at pressures to $600 \cdot 10^5$ Pa. The toluol λ values obtained agreed with the data of the most reliable experiments [3-6] to an accuracy not exceeding the total uncertainty of comparable results.

The Freons F-13V1 and F-23 used in the experiments were synthesized at the State Institute for Applied Chemistry. Impurity contents did not exceed 0.01 and 0.05%, respectively. The F-13V1 thermal conductivity was measured along isotherms at pressures of 1.0, 10.8, 15.7, 20.6, 30.4, 40.2, 50.0, 59.7, 74.5, 99.1, 197.1, 393.2, and $589.4 \cdot 10^5$ Pa, while the F-23 was measured at 1.0, 50.0, 197.1, 393.2, and $589.4 \cdot 10^5$ Pa. In calculating λ corrections were introduced for heat exchange by radiation, filament eccentricity, heat loss from device ends, and change in geometric dimensions of the measurement cell. To eliminate convective heat transfer all experiments were performed at two to four different temperature differentials in the layer, while the Rayleigh criterion in the parameter range studied (except for the near-critical region) did not exceed 1200. The maximum relative error of the λ data is estimated at ±1.2%.

With approach to the critical temperature on the isobars 40.2, 50.0, 59.7, and $74.5 \cdot 10^5$ Pa distortion of the measurements due to the presence of convection becomes unavoidable, so the experiments in this range were performed at relatively

TABLE 1. Experimental Values of Thermal-Conductivity Coefficient of Freon F-13V1, w/(m · deg)

t, °C	$\lambda\cdot10^4$	t, °C	$\lambda\cdot10^4$	t, °C	$\lambda\cdot10^4$	t, °C	$\lambda\cdot10^4$	t, °C	$\lambda\cdot10^4$	t, °C	$\lambda\cdot10^4$	t, °C	$\lambda\cdot10^4$	t, °C	$\lambda\cdot10^4$
$P=1,0\cdot10^5$ Pa		41,9	112,5	58,2	187,0	130,9	172,4	73,5	424	58,3	487	100,9	494	160,8	557
−167,9	1139	42,9	113,1	60,3	179,6	162,6	190,9	100,2	322	73,6	457	101,5	497	161,9	555
−167,4	1140	91,1	135,4	70,7	161,4	$P=50,0\cdot10^5$ Pa		100,9	314	73,9	460	129,7	467	$P=589,4\cdot10^5$ Pa	
−166,4	1135	91,9	136,1	87,8	156,6	0,2	588	130,3	231	87,2	432	130,4	462	−121,6	1136
−163,8	1131	157,1	167,3	109,6	163,0	0,8	590	131,3	233	101,1	423	161,2	434	−119,7	1129
−161,5	1121	158,3	167,3	110,5	164,3	39,9	481	$P=74.1\cdot10^5$ Pa		101,6	420	161,9	438	−83,8	1021
−150,6	1094	$P=15,7\cdot10^5$ Pa		131,4	170,4	40,8	476	−0,3	606	130,6	383	$P=393,2\cdot10^5$ Pa		−82,1	1017
−147,2	1085	−75,3	819	158,0	178,0	58,2	438	0,5	603	131,1	386	−151,2	1173	−43,6	910
−121,1	991	−74,3	814	162,5	181,4	59,3	436	40,4	503	$P=197,1\cdot10^5$ Pa		−149,6	1166	−42,4	907
−119,4	986	−43,7	704	$P=40,2\cdot10^5$ Pa		70,3	406	40,6	504	−157,5	1147	−123,1	1093	−5,1	821
−83,6	842	−42,8	701	0,3	581	70,4	409	58,5	462	−156,3	1151	−118,4	1082	−4,4	819
−81,9	838	−5,0	576	0,9	576	89,0	304	73,7	434	−151,1	1131	−83,9	967	−40,8	742
−72,1	801	−4,1	580	40,1	464	89,2	306	73,9	436	−147,5	1125	−82,6	964	41,6	745
−71,3	795	$P=20,6\cdot10^5$ Pa		40,3	467	99,8	229	80,6	417	−123,0	1052	−43,6	844	73,5	703
21,6	96,1	41,2	133,2	58,2	421	100,9	224	87,2	406	−118,1	1036	−42,5	845	74,6	707
23,7	97,9	42,6	137,5	58,3	424	130,9	201	100,8	384	−83,7	921	−4,9	737	101,5	682
41,1	105,9	50,6	129,9	70,3	359	131,0	202	101,0	381	−82,2	911	−3,7	742	102,0	684
42,0	106,4	51,7	130,3	70,4	354	$P=59,7\cdot10^5$ Pa		130,1	294	−43,9	776	41,0	664	129,8	665
80,5	126,2	84,9	140,2	73,9	279	−0,2	590	130,9	297	−42,6	780	41,9	670	131,4	659
81,5	126,5	85,7	140,8	74,2	278	0,7	594	$P=99,1\cdot10^5$ Pa		−4,7	674	73,4	624	160,6	648
157,5	166,0	130,9	160,1	80,3	214	40,3	490	0,4	612	−4,0	666	75,0	627	161,5	643
159,2	165,9	158,2	171,7	80,9	213	40,7	492	0,5	614	39,8	584	100,6	605		
$P=10,8\cdot10^5$ Pa		158,8	172,3	89,6	194,9	58,2	449	40,6	520	40,4	589	101,9	603		
21,9	104,7	$P=30,4\cdot10^5$ Pa		90,0	188,7	58,5	451	41,1	524	73,4	533	129,6	577		
23,4	105,7	56,2	202	101,2	179,1	70,6	426	57,8	484	73,7	529	131,0	580		

TABLE 2. Experimental Values of Thermal-Conductivity Coefficient of Freon F-23, w/(m · deg)

t, °C	$\lambda\cdot10^4$	t, °C	$\lambda\cdot10^4$	t, °C	$\lambda\cdot10^4$	t, °C	$\lambda\cdot10^4$
$P=1,0\cdot10^5$ Pa		−96,9	1482	−79,2	1433	−4,2	1101
−154,5	1826	−94,9	1470	−43,4	1199	−3,1	1092
−153,3	1817	−80,8	1356	−42,5	1199	$P=589,4\cdot10^5$ Pa	
−151,7	1808	−79,9	1351	−4,9	988	−147,4	1947
−149,9	1800	−43,1	1107	−3,7	976	−145,5	1937
−149,1	1793	−42,0	1093	$P=393,2\cdot10^5$ Pa		−144,0	1942
−147,1	1785	−4,8	843	−147,3	1891	−138,6	1915
−144,1	1766	−4,3	848	−146,1	1890	−136,6	1903
−142,1	1760	$P=197,1\cdot10^5$ Pa		−137,4	1856	−132,0	1872
−137,4	1729	−148,5	1847	−136,0	1844	−130,6	1868
−135,8	1721	−146,0	1840	−131,9	1820	−121,4	1839
−131,5	1696	−144,3	1825	−130,4	1812	−119,9	1822
−129,8	1685	−142,4	1819	−121,3	1760	−97,5	1701
−121,1	1616	−137,3	1798	−119,7	1752	−95,7	1695
−119,5	1613	−135,7	1782	−97,3	1628	−80,8	1607
−96,8	1458	−121,1	1692	−95,4	1621	−78,3	1593
−94,7	1452	−119,4	1693	−80,5	1521	−43,9	1395
$P=50,0\cdot10^5$ Pa		−97,1	1549	−77,8	1514	−43,0	1393
−121,1	1647	−95,1	1542	−43,9	1293	−4,8	1212
−119,6	1640	−80,8	1440	−43,0	1295	−2,8	1210

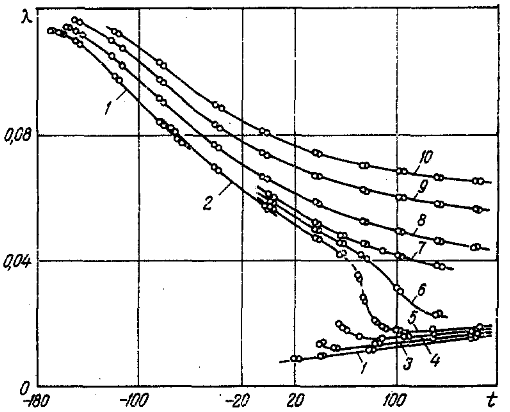

Fig. 2. Thermal conductivity, W/(m · deg), of Freon F-13V1 versus temperature: 1) 1.0; 2) 15.7; 3) 20.6; 4) 30.4; 5) 40.2; 6) 59.7; 7) 99.1; 8) 197.1; 9) 393.2; 10) 589.4 · 10^5 Pa.

low temperature differentials of 0.4 to 3°. It appears impossible to us to estimate the effect of convection, since data needed to calculate the Rayleigh criterion is lacking in the literature, in particular, the isobaric heat capacity of Freon 13V1 in the region of the maxima. Thus the error in the experimental λ data at temperatures of 58, 70, and 74°C on the isobars referred to is approximately estimated at ±3-5%.

It should be noted that of existing methods for experimental determination of the coefficient of thermal conductivity, only the plane-layer method can be used to study the thermal-conductivity maxima which occur in the critical region. Since the heated-filament method used in the present study does not produce reliable thermal-conductivity data in the critical region, we did not consider the range of anomalous λ behavior.

Experimental λ values for Freons F-13V1 and F-23 are presented in Tables 1 and 2, while the temperature dependence of F-13V1 thermal conductivity at pressures of 1.0, 15.7, 20.6, 30.4, 40.2, 59.7, 99.1, 197.1, 393.2, and 589.4 · 10^5 Pa is shown in Fig. 2. Since the literature offers no data on the effect of pressure on the crystallization temperature of Freons, detailed measurements of λ in the direct vicinity of the fusion point were performed only at atmospheric pressure.

Analysis of the experimental data revealed that with approach to the crystallization temperature the derivative $(\partial\lambda/\partial T)_p$ in Freons F-13V1 and F-23 decreased significantly on all isobars. Thus, for example, significant curvature of the temperature dependence of λ in Freon F-13V1 begins with a temperature of –120°C. Thus, the existing practice of determining the thermal-conductivity coefficient near the fusion temperature by extrapolation by a linear law can lead to a divergence of 7-8% from experimental data. A possible cause for this peculiarity in the temperature dependence of λ might be the appearance of traces of crystalline structure at some distance from the fusion point.

With increase in pressure the value of the derivatives $(\partial\lambda/\partial T)_p$ on the isotherms decreases, which is explained completely by shifting of the crystallization point in the direction of higher temperatures.

In attempting to analytically describe the results obtained, we took into consideration the fact that the most widely used forms of equations for thermal conductivity of gases and liquids are invariably connected with density data. The quite similar equations

$$\lambda = f(\rho) \text{ and } \Delta\lambda = f(\rho) \tag{1}$$

have received wide use [7, 8].

In a recently published study [9] a method was offered for construction of a thermal-conductivity equation for gases and liquids in the form of an equation in elementary functions:

$$\lambda(\omega, \tau) = f_1(\omega) + f_2(\omega)\tau + f_3(\omega)\lambda_0(\tau). \tag{2}$$

TABLE 3. Coefficients of Eq. (4)

	a_0	a_1	a_2	a_3
b_0	−12,64089	5,591012	− 6,009585	1,212197
b_1	36,06836	−20,03916	20,87071	−4,218974
b_2	−34,33817	25,62739	−25,86500	5,271006
b_3	13,20916	−12,42078	12,24743	−2,538179
b_4	0,5914344	− 0,1123499	0,1843546	−0,02417065
b_5	− 1,721998	1,838470	− 1,799844	0,3835580
b_6	0,3235089	− 0,3956934	0,3856990	−0,08462143

TABLE 4. Coefficients of Eq. (5)

	A_0	A_1	A_2	A_3
B_0	−12,32839	4,044646	− 6,758868	1,213438
B_1	34,97512	−14,57781	23,50252	−4,222433
B_2	−32,36364	18,66259	−29,21454	5,274969
B_3	12,56928	− 8,969806	13,92564	−2,540878
B_4	0,5298200	− 0,09169575	0,1377846	−0,2293085
B_5	− 1,586305	1,291087	− 2,040414	0,3832098
B_6	0,2952764	− 0,2699053	0,4414892	−0,08457882

The equation obtained in [9] for λ of nitrogen is notable for its high accuracy.

Altunin and Sakhabetdinov [10] recommend a number of promising equations of the type $\lambda = f(\omega, \tau)$ for calculation of thermal-conductivity coefficients with use of a computer. Without degrading the value of these equations, it must be noted that their application is limited by a number of inherent difficulties. These are connected, on the one hand with the appearance of isotherm layering in λ, ρ coordinates, which in a number of cases makes it impossible to employ equations of the form of Eq. (1). On the other hand, there are not always available detailed data on gas and liquid densities, these, in turn, being complex functions of temperature and pressure. Thus it is quite justifiable to attempt to obtain an equation for thermal conductivity as a function of temperature and pressure, parameters which are directly measurable in experiments.

Study of the behavior of isobars and isotherms of thermal conductivity shows that far from the critical region they have a quite simple form. Making use of this fact, a number of authors have proposed several equations for this region, and [11] recommended a method for construction of such an equation at high values of state parameters. Rivkin [12] attempted to extend the range of such an equation to the critical region, proposing an approximation of the constant thermal-conductivity line λ = const in P, T coordinates. Studying the thermal conductivity of water in the critical region Rivkin noted [12] that at certain state parameters the lines λ = const are straight:

$$T = f_1(\lambda) + Pf_2(\lambda). \tag{3}$$

Rivkin then notes that if with time more accurate experimental data on thermal conductivity of water in the critical region are obtained and the linearity of λ = const in P, T coordinates is found not to hold, then the proposed method may still prove useful. Terms may be added to Eq. (3) of higher order (for example, second) in pressure with coefficients dependent on λ.

The analysis performed in the present study of λ in Freon F-13V1 over a wide range of state parameters also showed that the simplest configuration of the various λ, P, T surfaces is shown by lines of constant thermal conductivity. While being straight in the liquid region, upon approach to the critical region these lines begin to curve markedly, and even show a maximum in the superheated vapor region (the derivative $[\partial P/\partial T]_\lambda$ changes sign). Since the majority of experimental λ points for Freon F-13V1 were obtained in the liquid region, we followed the recommendations of [12] as to supplementing Eq. (3) by higher-order terms in P, with the result

$$\frac{T}{100} = a_0 + a_1\left(\frac{P}{100}\right) + a_2\left(\frac{P}{100}\right)^2 + a_3\left(\frac{P}{100}\right)^3, \tag{4}$$

where the coefficients a_i are functions of λ, $a_i = \sum_0^6 b_j\left(\frac{1}{10\lambda}\right)^j$.

A shortcoming of such an equation is that it is insensitive to transition across the elasticity curve and will give false λ values at $P < P_s$. Considering the specifics of Freons as working substances in cooling apparatuses, where thermophysical data near the saturation line are especially important, another form of this equation can be recommended:

$$\frac{T}{100} = A_0 + A_1\left(\frac{P-P_s}{100}\right) + A_2\left(\frac{P-P_s}{100}\right)^2 + A_3\left(\frac{P-P_s}{100}\right)^3. \tag{5}$$

Such a form, also valid only for $P > P_s$, will obviously give more accurate values near the elasticity curve, inasmuch as the contribution of the terms containing A_1, A_2, and A_3 levels in this region, while the coefficient A_0, being in essence a function of $T = f(\lambda_s)$, may be directly determined from experimental data.

Determination of the thermal-conductivity coefficient from Eqs. (4) and (5) requires several iterations, since they contain λ implicitly. Solution of Eq. (5) is somewhat more complex, since for each given λ it is necessary to find T_s, then P_s, and only then T; however, with use of a computer such an approach offers no special difficulties.

Data on the Freon F-13V1 elasticity curve were taken from [13], which offers, aside from tabular data, coefficients of an approximating polynomial. Equations (4) and (5), whose coefficients are given in Tables 3 and 4, describe our experimental data on λ of Freon F-13V1 to the point $\lambda = 0.40$ W/(m · deg) with an error significantly exceeding the accuracy of the experimental data only at pressures of $400\text{-}600 \cdot 10^5$ Pa.

It should be noted that the superheated vapor region cannot be described by equations such as Eqs.(4) or (5).

NOTATION

λ, coefficient of thermal conductivity; T, temperature; P, pressure; ρ, density; $\Delta\lambda$, excess thermal conductivity; ω, reduced density; τ, reduced temperature; λ_0, thermal conductivity at atmospheric pressure; P_s, saturation pressure; T_s, saturation temperature; a, b, A, B, coefficients.

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