TRANSFER PROPERTIES OF FREON-22 VAPOR

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Experimental data on heat conduction are discussed from the point of view of their analysis together with other transfer coefficients to obtain more reliable information.

The thermal conductivity of Freon-22 vapor, one of the widely distributed working substances of refrigeration engineering and chemical technology, is measured in the temperature range of 237-423°K. An absolute variant of the stationary hot-filament method [1] is used. The measurement cell, made of Pyrex glass, had the following main characteristics: diameter of platinum filament 0.1000 ± 0.005 mm; thickness of layer of test gas 1.465 ± 0.005 mm; length of measurement section of filament 130.2 ± 0.1 mm. The quality of the platinum used in resistance thermometers was characterized by the ratio of the resistances at the boiling point and at the triple point of water, which was 1.3919 and 1.3918 for the outer and inner thermometers, respectively. The thermometers were calibrated in the thermometric laboratory of the D. I. Mendeleev All-Union Scientific-Research Institute of Metrology. The content of the main product in the investigation of Freon-22, synthesized at the State Institute of Applied Chemistry, was 99.98% according to the analysis data.

We obtained 17 experimental values of the thermal conductivity (Table 1) at pressures close to atmospheric.

We allowed for all the corrections inherent to the hot-filament method, as well as the possible contribution of accommodation, convection, and radiation [2]. Starting from the experience of previous work on the thermal conductivity of Freon-22, the error of the results obtained was estimated very thoroughly. The confidence coefficient was taken as 0.95; in this case the limiting random error proved to equal 0.37%, while the unexcluded remnant of the systematic error was 0.84%. The maximum relative error of the test data was estimated as ±0.92%. The correctness of the author's estimate of the error was confirmed by comparing control tests on determining the thermal conductivity of gaseous argon with the recommended values in the fundamental handbook [3].

Seven experimental reports on the thermal conductivity of Freon-22 vapor are known. In each of them the error of the data obtained was estimated as 1.0-2.5%. A more detailed acquaintance with these reports showed that not all the groups of experimental data are equally reliable, and that there are significant disagreements in the results of independent measurements. At this point it seemed important to elevate the degree of reliability of the analysis, to branch out from the particular set of data obtained by us to examine the entire volume of initial information, including the use of test data on diverse kinetic characteristics.

We examined the results of [4-10], including 56 experimental values of the thermal conductivity (with allowance for the data of the present work). The array of initial data on the viscosity, just as in [11], comprised 43 test points in the range of 233-473°K. The information on viscosity was supplemented by the new work of Kestin and Wakeham (five points) [12] and Latto [13] (eight points).

Statistical weights were assigned to the experimental data on the basis of the results of the analysis of each group of measurements. For viscosity the highest priority was given to the work of Kestin and Wakeham, Latto, and Butyrskaya; for thermal conductivity the groups of data obtained by Masia, Gruzdev, Geller, and their colleagues, and in the present work were among the primary data.

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TABLE 1. Experimental Values of Thermal Conductivity $\lambda \cdot 10^5$, W/(m·°K)

t, °C	—35,18	—35,17	—27,55	—13,59	—13,58	5,06
λ	719	723	759	841	840	946
t, °C	5,06	46,64	46,63	81,62	83,05	83,08
λ	947	1194	1196	1414	1428	1429
t, °C	127,72	128,20	150,25	150,25	151,40	
λ	1751	1750	1875	1880	1910	

After a mathematical analysis of the entire set of reliable measurements on thermal conductivity and viscosity we obtained the equations

$$\lambda \cdot 10^5 = 9{,}44763 \cdot 10^{-2} T^{1{,}637} - 968{,}3 \exp\left(-\frac{2{,}7329 \cdot 10^8}{T^3}\right) \tag{1}$$

for thermal conductivity in the temperature range of 233-433°K and

$$\eta \cdot 10^8 = 84{,}3502 + 3{,}1026T + 5{,}3402 \cdot 10^{-3} T^2 - 8{,}9175 \cdot 10^{-6} T^3 + 3{,}8125 \cdot 10^{-9} T^4 \tag{2}$$

for viscosity in the temperature range of 233-473°K. Recommended values of the coefficients of viscosity and thermal conductivity calculated from Eqs. (1) and (2) are given in Table 2. The generalized results are compared with experiment in Figs. 1 and 2. The values of the viscosity and thermal conductivity determined by calculation were taken as the frame of reference. According to our estimate, a limiting error of 2% for the thermal conductivity and close to 1% for the viscosity must be assigned to the data of Table 2 within the investigated temperature ranges.

The tabular data of [3] coincided with the recommended values of the thermal conductivity at 243°K, they proved to be somewhat lower than the latter at 353°K, by 1.3%, and 3.4% lower at 433°K (Fig. 1). These disagreements do not go beyond the tolerance zone of the estimated error of [3]. It is seen from Fig. 2 that the generalized values of the viscosity are oriented toward the new test data, being in good agreement with the tables of [11], as well as [14, 15].

The calculated values of the dimensionless complex (the Eucken factor) $f = \lambda M/\eta C_v$ are presented in Table 2.

The following connection between the kinetic coefficients [16] results from the character of the variation of f with temperature:

$$\varkappa = \eta^* = \Phi(\tau), \tag{3}$$

where

$$\varkappa = \frac{\lambda/C_v}{(\lambda/C_v)_{cr}}, \tag{4}$$

$$\eta^* = \eta/\eta_{cr}. \tag{5}$$

An analytical expression for the function Φ in Eq. (3) was found from the results of a joint analysis of test data on viscosity and thermal conductivity in the generalized coordinates defined by Eqs. (4) and (5). To strengthen the extrapolation possibilities of Eq. (3), we used the following considerations. The equation for the viscosity suggested by the modern molecular-kinetic theory of rarefied gases has the form

$$\eta = 2{,}6693 \cdot 10^{-6} \sqrt{MT}/\sigma^2 \Omega^{(2,2)}(T^*). \tag{6}$$

Then, with allowance for (5) and (6), we obtain

$$\Phi(\tau) = \frac{\Omega^{(2,2)}(T^*_{cr})}{\Omega^{(2,2)}(T^*)} \tau^{1/2}. \tag{7}$$

TABLE 2. Properties of Freon-22

T, °K	$\lambda \cdot 10^5$, W/(m·°K)	$n \cdot 10^8$, Pa·sec	C_V, kJ/(kg·°K)	f	$D_{11} \cdot 10$, cm^2/sec
233,15	710	996	0,475	1,501	0,297
243,15	760	1040	0,487	1,501	0,323
253,15	812	1083	0,499	1,502	0,350
263,15	865	1126	0,512	1,501	0,378
273,15	920	1170	0,524	1,501	0,407
283,15	976	1213	0,536	1,501	0,438
293,15	1033	1256	0,548	1,501	0,469
303,15	1091	1299	0,559	1,501	0,501
313,15	1150	1342	0,571	1,501	0,535
323,15	1211	1385	0,582	1,501	0,569
333,15	1273	1428	0,594	1,501	0,605
343,15	1335	1470	0,605	1,502	0,641
353,15	1399	1513	0,616	1,502	0,679
363,15	1463	1554	0,626	1,502	0,717
373,15	1528	1596	0,637	1,502	0,756
383,15	1593	1638	0,648	1,502	0,796
393,15	1659	1679	0,658	1,502	0,837
403,15	1725	1720	0,668	1,502	0,879
413,15	1791	1760	0,678	1,501	0,922
423,15	1857	1800	0,688	1,500	0,965
433,15	1923	1840	0,697	1,500	1,009
443,15	1993	1879	0,706	1,502	1,054
453,15	2061	1918	0,716	1,501	1,100
463,15	2128	1956	0,724	1,502	1,146
473,15	2195	1994	0,733	1,501	1,194
483,15	2263	2032	0,742	1,501	1,242
493,15	2330	2069	0,750	1,501	1,290
503,15	2397	2106	0,758	1,502	1,339
513,15	2463	2142	0,766	1,501	1,389
523,15	2529	2178	0,773	1,502	1,439
533,15	2594	2213	0,781	1,501	1,490
543,15	2659	2248	0,788	1,501	1,542
553,15	2723	2282	0,795	1,501	1,594

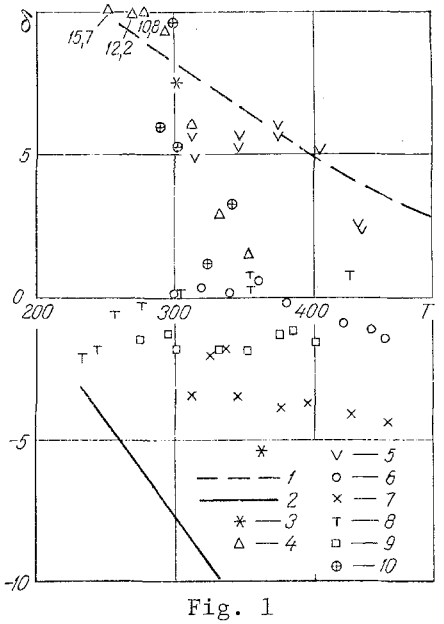

Fig. 1

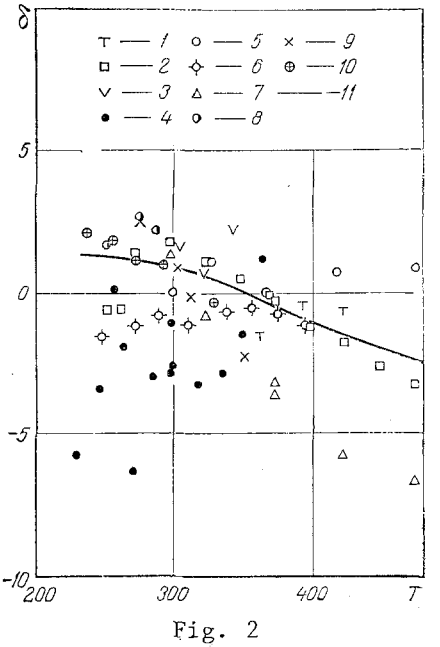

Fig. 2

Fig. 1. Comparison of recommended values of thermal conductivity with experimental data and a calculation from Eqs. (9) and (10): 1) Calculation from Eq. (10); 2) from (9); 3) data of [5]; 4) [4]; 5) [6]; 6) [7]; 7) [8]; 8) present work; 9) [9]; 10) [10]. δ, %; T, °K.

Fig. 2. Comparison of recommended values of viscosity with experimental data: 1) Tsui; 2) Butyrskaya; 3) Kam'en, 4) Latto, Hesuni, and Ashrani; 5) Kestin and Wakeham; 6) Latto; 7) Makita; 8) Wilbers; 9) Benning and Markwood; 10) Coflin; 11) [11].

The values of the collision integrals in (7) can be calculated if the parameters of the intermolecular interaction potential are known. These parameters were determined from viscosity data for two potentials, Lennard-Jones 12:6 and Stockmayer, and an effective collision integral proposed by Kestin, Ro, and Wakeham (KRW) [12]. The respective results proved to be: σ = 4.647 Å and ε/k = 283.8°K; σ = 4.597 Å, ε/k = 291.9°K, and δ = 0.25; σ = 4.596 Å and ε/k = 303.1°K.

The maximum and rms deviations of the calculations based on (6) from tabular data for the Lennard-Jones 12:6 potential were 0.24 and 0.14%, respectively, for the Stockmayer potential 0.29 and 0.18%, and for the KRW effective potential 0.15 and 0.09%. Since the most physically well-founded potential for polar molecules, which include Freon-22, is the Stockmayer potential, it was used in the further calculations.

On the basis of the foregoing, the function Φ was approximated by the polynomial

$$\Phi(\tau) = 0{,}05342 + 0{,}7256\tau + 0{,}4612\tau^2 - 0{,}2844\tau^3 + 0{,}0449\tau^4. \quad (8)$$

The values of the thermal conductivity in the temperature range of 433-553°K and of the viscosity in the range from 473 to 553°K were calculated using (8) (Table 2).

The heat capacity in the ideal-gas state was taken from Bahro's data with allowance for a correction for the anharmonicity of the vibrations [17]. The values of the thermal conductivity and viscosity at the critical temperature found from the results of a statistical analysis of the experimental data were η_{cr} = (1579.0 ± 15.2)·10^{-8} Pa·sec and λ_{cr} = (1502.0 ± 16.1)·10^{-5} W/m·°K.

The Eucken factor can be determined from the well-known theoretical equations proposed for monatomic gases by Eucken [18]

$$f_E = 1 + \frac{9R}{4C_v}, \quad (9)$$

Hirschfelder [18]

$$f_H = F + \frac{3R}{2C_v} L, \quad (10)$$

and Mason and Monchick [19]

$$f_{MM} = F + \frac{3}{2} L \frac{R}{C_v} - \frac{1}{2} L^2 \sum_k \frac{\eta C_{vk}}{P\tau_k C_v}, \quad (11)$$

where

$$F = \rho D/\eta; \; L = \frac{5}{2} - F.$$

The relaxation time is usually expressed through the number of collisions $Z = \tau/\tau_c$, where τ_c is the mean time between successive collisions, $\tau_c = \pi\eta/4P$.

The results of calculations of the thermal conductivity of Freon-22 using Eqs. (9) and (10) are presented in Fig. 1. As seen from the figure, Eq. (9) gives understated results, whereas the values of the thermal conductivity calculated from Eq. (10), as the theory predicts, serve as a unique "ceiling" in the terminology of [20].

A significant difficulty in calculations by the Mason–Monchick equation, which allows for the contribution of inelastic collisions, in contrast to (10), is the determination of the relaxation time. No experimental information on this question for Freon-22 is known in the literature. The relaxation time (or the number of collisions, which is the same) was calculated from data on thermal conductivity. The coefficient of diffusion of internal energy was taken as equal to the coefficient of self-diffusion [19] on the basis of a number of assumptions: 1) the role of inelastic collisions for the vibrational degrees of freedom can be neglected [19]; 2) considering the slight reduced dipole moment of the Freon-22 molecule, no correction was introduced into the value of the coefficient of diffusion for resonance exchange [21].

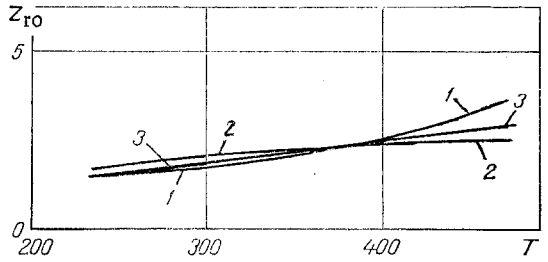

Fig. 3. Values of the numbers of collisions for rotational relaxation, calculated: 1) from (11); 2) from (12); 3) from (13).

Values of the numbers of collisions for rotational relaxation, obtained from Eq.(11), are presented in Fig. 3. In the same graph we plot the results of calculations of the numbers of collisions by the theoretical equation of Sather and Dahler [22]

$$Z_{ro}^{-1} = \frac{5\pi}{12} \frac{4I/m\sigma_\eta^2}{[1+(4I/m\sigma_\eta^2)]^2} \exp(\varepsilon/kT) \tag{12}$$

and Parker's theoretical equation corrected by Brau and Jonkman [23]

$$Z_{ro} = Z_{ro}^{\infty}\left[1+\frac{\pi^{3/2}}{2}\left(\frac{1}{T^*}\right)^{1/2}+\left(\frac{\pi^2}{2}+2\right)\frac{1}{T^*}+\pi^{3/2}\left(\frac{1}{T^*}\right)^{3/2}\right]^{-1}, \tag{13}$$

where $\sigma_\eta^2 = \sigma^2\Omega^{(2,2)}(T^*)$; $T^* = T/\varepsilon/k$. In the latter case the limiting value of the number of collisions was detemrined from data on thermal conductivity and proved to equal 25.2. This number agrees well with that recommended for methane, 32.5 [19]. On the whole, as seen from Fig. 3, fully satisfactory agreement is obtained, both on the character of the temperature dependence and on the absolute values of the numbers of collisions. The disagreements increase with an increase in temperature, but in this region the inaccuracy in knowing the number of collisions has a very weak effect on the final result, since the relative share of the correction term, which includes the number of collisions, is only a few percent.

The kinetic theory permits a calculation of the coefficient of self-diffusion for molecules possessing spherical symmetry [18]. The Freon-22 molecule is not spherically symmetric, strictly speaking, and therefore the coefficient of self-diffusion was calculated from a somewhat altered relation using equations of the theory for the viscosity and the coefficient of diffusion [18]:

$$D_{11} = 9.9764\cdot 10^7 \frac{\Omega^{(2,2)}(T^*)}{\Omega^{(1,1)}(T^*)} \frac{T\eta}{PM}.$$

The ratio of the collision integrals depends weakly on temperature [18] and has about the same value for many models of potentials.

The calculated values of the coefficient of self-diffusion are presented in Table 2. Since no test data on this coefficient were available to us, the tabular values can be considered as provisional.

NOTATION

P, pressure, 0.1 MPa; C_{vk}, translational, rotational, and vibrational components of heat capacity; τ_k, relaxation time; η, coefficient of dynamic viscosity; λ, coefficient of thermal conductivity; τ, reduced temperature; T, temperature, °K; M, molecular mass; ρ, gas density; D, coefficient of diffusion of internal energy; R, universal gas constant; σ, ε/k, parameters of the intermolecular interaction; I, moment of inertia of a molecule; $\Omega^{(2,2)}(T^*)$, collision integrals; D_{11}, coefficient of self-diffusion; Z, number of collisions; $\delta = (\lambda_{exp} - \lambda_{tab})/\lambda_{tab}$, relative deviation of data on thermal conductivity (similarly for viscosity). Index cr, value of a quantity at the critical temperature.

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