THE THERMAL CONDUCTIVITY OF GASEOUS DIFLUORODICHLOROMETHANE

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We present experimental data on thermal conductivity of difluorodichloromethane in the gaseous phase. The results of this investigation are compared with the data of the Mason–Monchick theory.

The thermal conductivity of monatomic gases and their mixtures can be calculated on the basis of the rigorous Chapman–Enskog theory [1]. However, for polyatomic gases (polar and nonpolar) the classical theory is not suitable. We know the empirical Eucken expression for the determination of the coefficient of thermal conductivity for polyatomic gases is

$$\frac{\lambda\mu}{\eta c_v} = 1 + \frac{9}{4}\frac{R}{c_v}. \tag{1}$$

A more rigorous analysis of the phenomenon, with the assumption that the transfer of the internal energy comes about as a consequence of molecular diffusion, leads to the so-called Hirschfelder–Eucken correction:

$$\frac{\lambda\mu}{\eta c_v} = \frac{\rho D_{\parallel}}{\eta} + \frac{3}{2}\frac{R}{c_v}\left(\frac{5}{2} - \frac{\rho D_{\parallel}}{\eta}\right) = f_{\text{H-E}} \tag{2}$$

where

$$\frac{\rho D_{\parallel}}{\eta} = \frac{6}{5}\frac{\Omega^{(2,2)*}}{\Omega^{(1,1)*}}. \tag{3}$$

To provide for the transfer of energy as a result of inelastic molecular collisions, Mason and Monchick [2] introduced the characteristic time into expression (2) – the time needed to establish equilibrium between the energies of the translational and the internal degrees of freedom. For nonpolar molecules we thus have

$$f_{\text{M-M}} = \frac{\lambda\mu}{\eta c_v} = \frac{1}{c_v}\left\{f_{\text{Г–Э}} - \frac{2}{\pi}\left(\frac{5}{2} - \frac{\rho D_{\parallel}}{\eta}\right)^2\left[\frac{c_{v\text{rot}}}{Z_{\text{rot}}} + \frac{c_{v\text{osc}}}{Z_{\text{osc}}}\right]\right\}. \tag{4}$$

If we bear in mind that z_{osc} is so large for all gases that in calculating thermal conductivity we need not make provision for oscillatory relaxation, and that

$$c_{v\text{rot}} = \frac{3}{2}R,$$

from Eq. (4) we will obtain

$$Z_{\text{вр}} = \frac{3}{\pi}\left(\frac{5}{2} - \frac{\rho D_{\parallel}}{\eta}\right)^2 \frac{R}{c_v}\,[f_{\text{H-E}} - f_{\text{M-M}}]^{-1}. \tag{5}$$

Since the direct measurements of Z_{rot} and calculation of this quantity from theoretical premises are not sufficiently reliable [3], and since such data are entirely unavailable for most substances, the values of Z_{rot} in this paper have been calculated for difluorodichloromethane at various temperatures, with

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consideration of (5) and the expression

$$f_{M-M} = f_{\exp} = \frac{\lambda_{\exp}\mu}{\eta c_v}. \quad (6)$$

We chose a method of vertical coaxial cylinders under conditions of a regular regime of the first kind [4] to measure the coefficient of thermal conductivity. The inside cylinder had a diameter of 14.687 mm and a length of 109.9 mm. The clearance between the outside and inside cylinders was 0.211 mm. The cylinders were kept coaxial by means of six Teflon pins. The pins were set into the inside cylinder and then machined on a lathe to the required size.

The inside cylinder has a center hole for a heater and three peripheral holes to house the junctions of differential thermocouples. The heater is made of a constantan wire whose diameter is 0.2 mm, passed into the orifice of a two-channel porcelain tube. The thermocouple is made of copper and constantan, with a diameter of 0.25 mm. The cold thermocouple junctions are positioned in the orifices drilled into the outside cylinder, near its inside surface. All of the thermocouple junctions are kept under pressure and they are thoroughly insulated.

There are two metal cylinders at each of the ends of the inside cylinder. The space between the center and side cylinders is 0.211 mm. The side cylinders are not insulated, and in calculating the constant of the instrument we must take into consideration the transfer of heat through the side surfaces. Relative to the side surface, the area of the two ends amounted to about 6.5%. All of the cylinders were fabricated of copper.

The instrument constant – determined from the results of the measurements and by weighing – amounted to 22.86 J/deg at 20°C.

The heat capacity of copper is taken from the Kay and Laby handbook [5]. We should take note of the fact that while at a temperature of ~20°C the heat-capacity data for technically pure copper coincide within the limits of tenths of a percent, at 100°C the heat-capacity values published in various handbooks diverge by several percent, which results in the same order of divergence for the values of the thermal conductivity. Removal of heat through the wiring of the thermocouples and the heater through the centering pins, the errors associated with the possible eccentricity in the positioning of the cylinders, particularly in view of the small space between the cylinders, all of this may serve to distort the data on the thermal conductivity. The values for the instrument constant were corrected on the basis of the above in accordance with the more reliable data on the thermal conductivity of air [6].

This correction factor increases with a rise in temperature, but does not exceed 4%.

The installation was designed with external thermostating. Since the accuracy with which temperature is maintained in a TS-24 thermostat is inadequate, temperature stabilization is achieved with a U-6 thermostat, series-connected to the TS-24 thermostat. With such a thermostating circuit we can maintain the temperature with an error of no more than ±0.005°C.

The evacuated installation is first filled with the material to be tested. The difluorodichloromethane is recondensed from a tank into an intermediate vessel, and from the latter, directly into the installation. The liquid filling the installation is subsequently evaporated. This operation is repeated several times. To monitor the results, and to observe the effect of admixtures of air or other gases, the installation is also filled by freezing the difluorodichloromethane in the intermediate vessel, and thoroughly evacuating the installation. Within the limits of measurement accuracy, the results proved to be identical.

In all other respects, the methods used in the experiment and processing of the measurement results correspond to those described earlier in [4].

In measuring the thermal conductivities of gases we find that two phenomena may prove to be exceedingly important: accommodation and the transfer of heat by radiation. With an increase in the density of the gas being investigated, i.e., with a reduction in the molecular mean free path, the effect of accommodation is substantially reduced. Nevertheless, its significance is proportional to the temperature gradient in the layer being studied. The phenomenon of accomodation is thus particularly dangerous in measuring cells in which the temperature gradient is very great. Bearing in mind the design of our instrument – used in the measurements – we might suppose that the effect of the temperature jump has been weakened to a considerable extent. An experimental test of this assumption was undertaken with measurements at

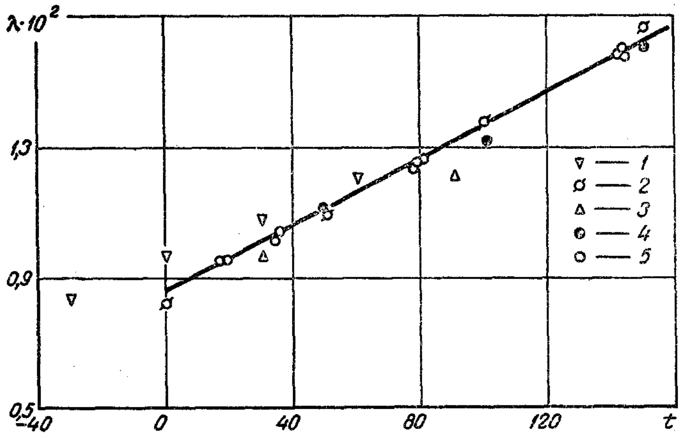

Fig. 1. The thermal conductivity of difluorodichloromethane at atmospheric pressure (t in °C; λ in W/m · deg): 1) the data of Cherneeva [8]; 2) the data of Sherratt and Griffiths [7]; 3) the data of Markwood and Benning [9]; 4) the data of Keyes [6]; 5) the data of the Leningrad Technology Institute of the Refrigeration Industry.

pressures ranging from 8 bar to atmospheric pressure, so that the error resulting from the accommodation of the gas varies in a relationship that is virtually proportional to the change in pressure.

An examination of the curve showing the thermal conductivity as a function of pressure reveals no singularities for this function near atmospheric pressure. To reduce the contribution of radiative heat transfer through the layer of the material being investigated, the cylinders were carefully machined, a layer of chromium was subsequently applied, and the surface polished. Calculation of the possible error leads to values of 0.73% at 500°K; the error at 400°K is 0.45%, and at 300°K it is 0.32%. The value of emissivity for the total normal radiation in the case of burnished copper was assumed to be 0.05.

The correction factor for the temperature difference across the walls of the inside and outside cylinders for small values of the clearance thickness may be quite substantial, particularly for substances exhibiting relatively high thermal conductivity. For thermal conductivities of $\lambda = 0.01\text{-}0.03$ W/m · deg in the materials which we investigated, the total temperature difference across the cylinder walls, respectively, did not exceed $(1\text{-}3) \cdot 10^{-3}$ of a fraction of the temperature difference across the gas layer.

We paid no attention to the transfer of heat by convection, since the Rayleigh number did not exceed 600, nor did we consider the collection factor for the heat capacity of the gas layer and the heating of the outside cylinder in the presence of a liquid thermostat. The cooling rates were measured with an M195/1 mirror galvanometer. Particular attention was devoted to protection against possible spurious thermal emf's. With this purpose in mind, the hot and cold junctions of the differential thermocouple were kept under pressure, the connection tubes of the thermocouples were thoroughly insulated, and they were shielded. In addition, we used a shielding circuit that was insulated both from the measuring circuit and from the ground. The circuit was initiated at the housing of the calorimeter, and it then was followed by shielded wiring and the metallic housing of the galvanometer.

The cooling-rate values derived experimentally were ~0.015-0.005 $\sec^{-1}$.

For the temperature of the meterial being studied we took the average between the temperatures of the two surfaces bounding the gas layer. The differences between the experimental and the smoothed values of the thermal conductivity amounted to ±1.2%, on the average.

Figure 1 compares the derived data with the measurement results of other authors. First of all, we should note that the differences among the existing data are substantially greater than the experimental error indicated by the cited authors. For example, at 0°C the error is ~16%, while at 90°C it is about 10%.

The results of this paper are in good agreement with the Keyes data [6] and the data of Sherratt and Griffiths [7] at normal temperatures. At higher temperatures, the data of [7] are somewhat higher, with the Keyes data correspondingly lower.

TABLE 1. Results of Calculations According to Eq. (5)

T, °K	$T^*=\frac{T}{\varepsilon/k}$	$\rho D_{\|\|}/\eta$	c_v	$\lambda_{\text{exp}}\cdot 10^3$	f_{exp}	Z_{rot}
293	1,302	1,319	63,94	9,588	1,473	2,27
313	1,391	1,317	66,47	10,562	1,465	2,27
333	1,480	1,318	68,55	11,538	1,465	2,40
353	1,569	1,315	70,57	12,513	1,462	2,53
373	1,658	1,316	72,42	13,487	1,462	2,65
393	1,747	1,314	74,17	14,463	1,459	2,81
413	1,836	1,313	75,74	15,437	1,460	3,08
433	1,924	1,313	77,21	16,412	1,462	3,36

The experience of previous investigations compels us to deal with extreme care in evaluating the accuracy of the derived results. The random errors are compared with the smoothed values of the thermal conductivity and amount to 1.2%.

We should also take into consideration the possible errors in the determination of the correction factor for the constant of the instrument in the experiments with air, as well as the error in conversion, the error in the time measurement, etc. Altogether this gives an evaluation for the measurement accuracy at about 2.5%. Considering the large number of errors and the low probability that they are all operative in the same direction, we can assume that the accuracy in measuring thermal conductivity will be higher.

The value of Z_{rot} is calculated from (5).

To calculate the complex in (3) we must know the collision integrals $\Omega^{(2,2)*}$ and $\Omega^{(1,1)*}$, whose values have been tabulated in [1] for various potentials. In the case of a system of nonpolar molecules, which are either spherical or virtually spherical in shape (this type of molecule includes the difluorodichloromethane molecule), we most frequently apply the Lennard–Jones 12 : 6 potential. Thus, to obtain the values of the collision integrals, we must have at our disposal the values of the force parameters σ and ε/k of this potential. The values of the parameters, calculated in various ways, may differ substantially; it is therefore desirable to use parameters determined with respect to viscosity for purposes of calculating the transport coefficients.

According to the Svehla data [10], for difluorodichloromethane $\sigma = 5.25$ Å and $\varepsilon/k = 253$°K.

The parameter values for the 12 : 6 potential, derived here from the experimental viscosity data [11, 12], amounted to $\sigma = 5.4$ Å and $\varepsilon/k = 225$°K and were used as the basis for subsequent calculations.

We took the heat capacity for the difluorodichloromethane from the Albright data of [13] and from the Masi data [14]. These data are in good agreement with each other, and the difference in the temperature interval of interest to us did not exceed 0.1%.

The results from the calculations of the number of collisions in the case of rotational relaxation are given in Table 1 . We see from the table that Z_{rot} increases with a rise in temperature. At the same time, the values of the factor f_{exp} and of the complex $\rho D_{||}/\eta$ vary quite insignificantly.

Finally, we note that these conclusions confirm the results obtained with respect to Z_{rot} for carbon dioxide [15] and ammonia [3].

NOTATION

λ	is the coefficient of thermal conductivity;
η	is the viscosity coefficient;
c_V	is the mole heat capacity;
μ	is the molecular mass;
R	is the universal gas constant;
$D_{\|\|}$	is the coefficient of self-diffusion;
ρ	is the gas density;
$\Omega^{(2,2)*}$ and $\Omega^{(1,1)*}$	are the collision integrals;
$c_{V\,\text{rot}}$ and $c_{V\,\text{osc}}$	are, respectively, the rotational and oscillatory capacities;
Z_{rot} and Z_{osc}	are, respectively, the numbers of rotational and oscillatory relaxation;
σ and ε/k	are force parameters.

LITERATURE CITED

1. J. Hirschfelder, C. Curtiss, and R. Bird, The molecular Theory of Gases and Liquids [Russian translation], IL (1961).
2. E. A. Mason and L. J. Monchick, Chem. Phys., 36, 1622 (1962).
3. V. N. Srivastava and A. Dasgupta, Phys. Fluids, 9, No. 4 (1966).
4. O. B. Tsvetkov, Inzh. Fiz. Zh., 9, No. 4 (1966).
5. D. Kay and T. Laby, Tables of Physical and Chemical Constants [Russian translation], Fizmatgiz (1962).
6. F. G. Keyes, Trans. ASME, 76, 5, 809 (1954).
7. G. G. Sherratt and E. Griffiths, Phil. Magazine, 27, 180, 68 (1939).
8. L. Cherneeva, in: Refrigeration Engineering [in Russian], Gostrogizdat (1953).
9. R. Plank, Handbutch der Kaltetechnik, 4 (1956).
10. R. A. Svehla, NASA, Technical Report, R 132 (1962).
11. T. Makita, Rev. Phys. Chem. Japan, 24, No. 2, 74 (1954).
12. O. W. Witzell and J. W. Johnson, Trans. ASHRAE, 71 (1965).
13. L. F. Albright and W. C. Galegar, J. Amer. Chem. Soc., 76, 6017 (1954).
14. J. F. Masi, J. Am. Chem. Soc., 74, 4738 (1952).
15. M. P. Vukalovich, V. V. Altunin, and V. V. Blinov, TFVT, 1, 356 (1963).