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Thermal Conductivity of Gaseous $CFCl_3$ (Freon 11) and CF_2Cl_2 (Freon 12) and Their Mixtures with N_2 at 292K

H. C. Peters,[1] J. N. Breunese,[1] and L. J. F. Hermans[1]

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Thermal conductivity of the gases $CFCl_3$ (Freon 11), CF_2Cl_2 (Freon 12), and their binary mixtures with nitrogen have been measured at 292 K. The results for the mixtures are compared with various theoretical models, which give the thermal conductivity as a function of concentration using properties of the pure components. From the experimental results, the mutual diffusion coefficients for the two systems are calculated.

KEY WORDS: $CFCl_3$–N_2 mixtures; CF_2Cl_2–N_2 mixtures; Freon; thermal conductivity.

1. INTRODUCTION

The relatively low thermal conductivity, λ, of $CFCl_3$ (Freon 11) and CF_2Cl_2 (Freon 12), as well as of their mixtures with nitrogen or air, is of interest for application of these gases in insulating foam. However, the literature data on λ for Freon 11 and Freon 12 have large uncertainties, while data on N_2–Freon 11 and N_2–Freon 12 mixtures are unavailable.[2] This makes thermal conductivity measurements for these systems desirable. Such measurements are also of interest to test the validity of the various approximations which predict thermal conductivity values for mixtures using properties of the pure components. Finally, these data yield a value for the mutual diffusion coefficient D_{12}, which has not been investigated to date.

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[1] Huygens Laboratory, University of Leiden, Wassenaarseweg 78, Leiden, The Netherlands.

[2] For the pure Freons see, e.g., Data book (Thermophysical Properties Research Cent., Purdue University, Lafayette, Ind., 1967), Vol. 2. Mixtures of Freon 11 with air were investigated recently by Tsvetkov and Laptev [1].

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2. EXPERIMENTAL

For data on the thermal conductivity of these systems to be useful for application in insulating materials, measurements should be performed at (or somewhat below) room temperature. Because of the high boiling points (297 and 243 K for Freon 11 and Freon 12, respectively), adsorption at the walls of the apparatus can be a serious drawback in this temperature region. This is the case especially in N_2–Freon 11 mixtures, where care must be taken to avoid errors in the composition of the mixture due to preferential adsorption of the Freon. Therefore, the measurements were performed in an apparatus essentially consisting of a gold plated cavity (approximately 5 cm^3 in volume) in a brass block, which was placed in a thermostated bath. In the center of the cavity, a thermistor was mounted serving both as thermometer and heat source. This thermistor (0.3 mm in

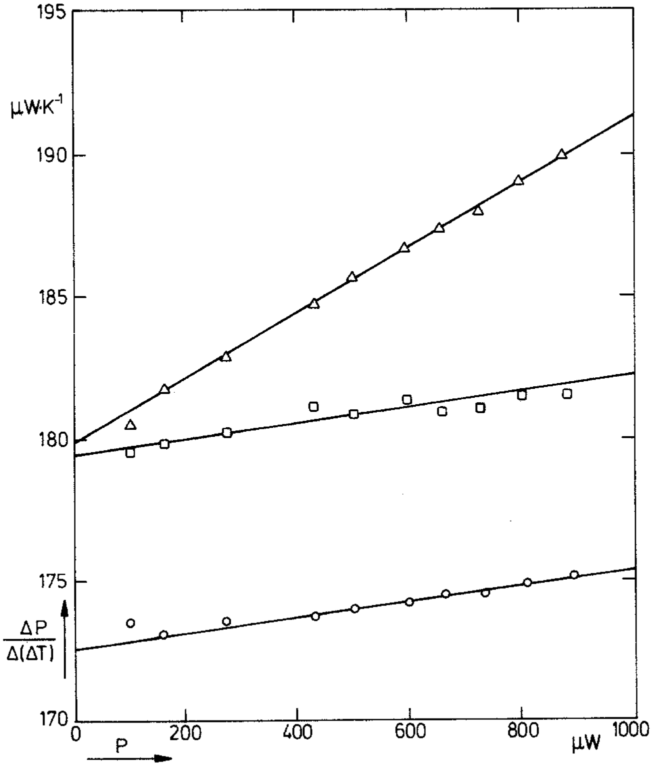

Fig. 1. Values of $\Delta P/\Delta(\Delta T)$ vs power P at different pressures p for pure Freon 12 ($T_b = 292$ K). △, $p = 102.1$ kPa (≈ 1 bar); □, $p = 26.1$ kPa; ○, $p = 0.31$ kPa. The highest pressure data suffer from convection, the lowest from mean free path effects.

diameter) is part of a Wheatstone bridge circuit with a variable dc voltage supply. By measuring the bridge voltage V and the resistance R of the thermistor, both its heating power P and its temperature T can be determined. If the difference between the thermistor temperature T and the bath temperature T_b is denoted by ΔT, the ratio $P/\Delta T$ bears a one-to-one relationship with λ for small ΔT.

Convection in the gas will increase the measured value of $P/\Delta T$. A convection free limit is approached by extrapolating to $\Delta T = 0$. This extrapolated value corresponds to the thermal conductivity at precisely the temperature T_b. In practice, however, a measurement of the true value of T_b is never achieved, because there is always some power dissipated in the thermistor when its resistance is measured, even at the minimum practical power P_0. Therefore, the temperature T_0, corresponding to P_0 (and thus slightly above T_b), is used as reference temperature. The ratio $\Delta P/\Delta(\Delta T)$, with $\Delta P = P - P_0$ and $\Delta(\Delta T) = T - T_0$, is then plotted versus P (see Fig. 1), and the extrapolated value for $P = 0$ is uniquely related to the thermal conductivity at the temperature of the bath T_b.

By repeating this procedure at different pressures, the extrapolated values can be compared to assess the influence of mean free path ("Knudsen") effects. Moreover, the slopes of the lines give an impression of the importance of convection. If no convection occurred, the slope would solely be determined by the temperature dependence, $d\lambda/dT$, of the thermal conductivity. From the low pressure limit of the slope in Fig. 1, a value $\lambda^{-1} \cdot d\lambda/dT = 4.4 \times 10^{-3}\mathrm{K}^{-1}$ is found for Freon 12, which is in good agreement with the literature value [1].

3. RESULTS AND DISCUSSION

In order to calibrate the apparatus, measurements were performed in a vacuum and on the reference gases Kr, CO_2, N_2, and Ne. A plot of the values of $(\Delta P/\Delta(\Delta T))_0$, i.e., the values of $\Delta P/\Delta(\Delta T)$ extrapolated to $P = 0$, as a function of the corresponding literature values for λ, yields a calibration. With this calibration, the unknown thermal conductivity for Freon 11 and Freon 12, as well as the mixtures, can be derived from the measured values of $(\Delta P/\Delta(\Delta T))_0$. This procedure was performed for two different cells in order to have a check on the reliability. The resulting values for the unknown λ's were found to agree within 2% in all cases. The values of λ for both the reference gases and the Freons and the mixtures are given in Table I. A plot of λ as a function of the Freon concentration is given in Fig. 2 for both systems studied. The experimental error is estimated to be smaller than 2%. For the N_2–Freon 11 system, an additional error of 3% in the concentration may be expected because of adsorption effects.

Table I. Thermal Conductivity in $mW \cdot m^{-1} \cdot K^{-1}$ for Mixtures of Freon 11 or Freon 12 with Nitrogen at 292 K[a].

		N_2-Freon 11 Mixtures			
	Measured	Calculated			
X_{Freon}	(this experiment)	[2][b]	[3][c]	[4][d]	[6][e]
0	25.40				
0.25	16.99	17.47	17.10	16.95	16.87
0.50	12.28	12.88	12.57	12.32	12.39
0.75	9.54	9.88	9.72	9.55	9.63
1	7.77				

		N_2-Freon 12 Mixtures			
	Measured	Calculated			
X_{Freon}	(this experiment)	[2][b]	[3][c]	[4][d]	[6][e]
0	25.40				
0.25	18.51	18.77	18.66	18.61	18.56
0.50	14.39	14.55	14.44	14.33	14.35
0.75	11.55	11.61	11.56	11.47	11.51
1	9.47				

[a] The reference gases were Kr ($\lambda = 9.20\ mW \cdot m^{-1} \cdot K^{-1}$), CO_2 ($\lambda = 16.02\ mW \cdot m^{-1} \cdot K^{-1}$), N_2 ($\lambda = 25.40\ mW \cdot m^{-1} \cdot K^{-1}$) and Ne ($\lambda = 48.5\ mW \cdot m^{-1} \cdot K^{-1}$). In all calculations, the first component was chosen to be N_2.

[b] With $G_{12} = 2.402$ and $G_{21} = 0.4345$ for N_2–Freon 11 mixtures and $G_{12} = 2.091$ and $G_{21} = 0.4963$ for N_2–Freon 12 mixtures.

[c] With $G_{12} = 2.761$ and $G_{21} = 0.3356$ for N_2–Freon 11 mixtures and $G_{12} = 2.339$ and $G_{21} = 0.3851$ for N_2–Freon 12 mixtures.

[d] With $\Lambda = 11.14\ mW \cdot m^{-1} \cdot K^{-1}$ for N_2–Freon 11 mixtures and $\Lambda = 13.42\ mW \cdot m^{-1} \cdot K^{-1}$ for N_2–Freon 12 mixtures.

[e] With $T^*_{12} = 1.66$, $A^*_{12} = 1.096$, $B^*_{12} = 1.137$, $D_{12} = 7.73 \times 10^{-6}\ m^2 \cdot s^{-1}$ for N_2–Freon 11 mixtures and $T^*_{12} = 1.83$, $A^*_{12} = 1.094$, $B^*_{12} = 1.127$, $D_{12} = 9.23 \times 10^{-6}\ m^2 \cdot s^{-1}$ for N_2–Freon 12 mixtures.

For a theoretical description of λ_{mix} as a function of concentration, many approximate formulas as found in the literature have the form:

$$\lambda_{\text{mix}} = \frac{\lambda_1}{1 + G_{12}(x_2/x_1)} + \frac{\lambda_2}{1 + G_{21}(x_1/x_2)} \tag{1}$$

with λ_i the thermal conductivity coefficient and x_i the mole fraction of the i component.

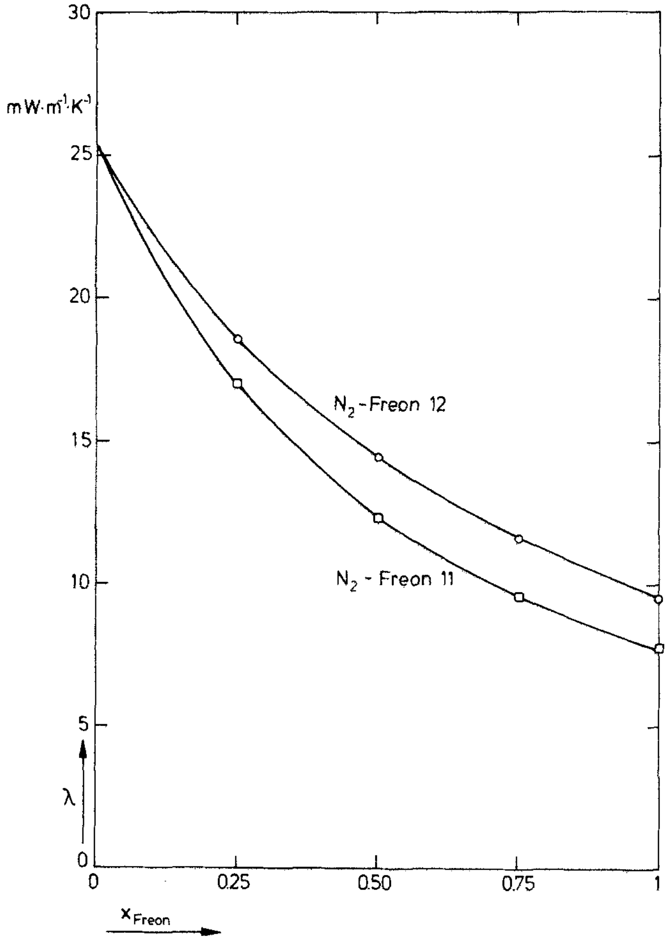

Fig. 2. Thermal conductivity of N_2–Freon 11 and N_2–Freon 12 mixtures at 292 K.

Lindsay and Bromley [2] suggest that

$$G_{ij} = \frac{1}{4}\left\{1 + \left[\frac{\eta_i}{\eta_j}\left(\frac{M_j}{M_i}\right)^{3/4}\frac{(1+(S_i/T))}{(1+(S_j/T))}\right]^{1/2}\right\}^2 \frac{(1+(S_{ij}/T))}{(1+(S_i/T))} \qquad (2)$$

with η_i the viscosity coefficient, M_i the mass, and S_i the Sutherland constant approximated by $S_i = 1.5T_{bi}$, where T_{bi} is the normal boiling point of the i component, while S_{ij} is the geometric mean of S_i and S_j, thus

$S_{ij} = \sqrt{S_i S_j}$. Equation (2) has been used to calculate the thermal conductivity for three compositions from Eq. (1), and the results are given in Table I. A comparison of these results with the experimental data shows that the calculations agree with experiment within 1.5% for N_2–Freon 12 mixtures and within 5% for N_2–Freon 11 mixtures.

Mason and Saxena [3] approximated G_{ij} by

$$G_{ij} = \frac{1}{2\sqrt{2}}\left(1 + \frac{M_i}{M_j}\right)^{-1/2}\left[1 + \left(\frac{\lambda_i^{\mathrm{mon}}}{\lambda_j^{\mathrm{mon}}}\right)^{1/2}\left(\frac{M_i}{M_j}\right)^{1/4}\right]^2 \tag{3}$$

with $\lambda^{\mathrm{mon}} = \frac{5}{2}\eta\bar{c}_v$ and $\bar{c}_v = \frac{3}{2}R/M$ (R is the gas constant). The results of this approximation are also given in Table I, and they agree with experiment within 2% in all cases.

If the thermal conductivity is known for at least one mixture, we can, according to Mason and Von Ubisch [4], write $G_{ij} = \lambda_i/\Lambda$, where Λ is a parameter that can be determined from the experimental data by a fitting procedure. This procedure was performed for both systems using the data at the three concentrations studied. The results of these calculations, as given in Table I, agree with experiment within 1%.

The most sophisticated description was given by Monchick et al. [5] for polyatomic gas mixtures. They showed that inelastic collisions only shift the curve but do not change its shape: if the λ_{mix} curve is anchored at its end points, then the simple Hirschfelder–Eucken formula is adequate:

$$\lambda_{\mathrm{mix}} = \lambda_{\mathrm{mix}}^{\mathrm{mon}} + \lambda_{\mathrm{mix}}^{\mathrm{int}} \tag{4}$$

Here

$$\lambda_{\mathrm{mix}}^{\mathrm{mon}} = 4\begin{vmatrix} L_{11} & L_{12} & x_1 \\ L_{21} & L_{22} & x_2 \\ x_1 & x_2 & 0 \end{vmatrix} \Bigg/ \begin{vmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{vmatrix} \tag{5}$$

with

$$L_{11} = -4\frac{x_1^2}{\lambda_1^{\mathrm{mon}}} - \frac{16}{25nRD_{12}}\,\frac{x_1x_2}{(M_1 + M_2)^2}$$
$$\times\left(\frac{15}{2}M_1^2 + \frac{25}{4}M_2^2 - 3M_2^2B_{12}^* + 4M_1M_2A_{12}^*\right)$$

(L_{22} is obtained from the expression for L_{11} by interchanging the subscripts) and

$$L_{12} = L_{21} = \frac{16}{25nRD_{12}} \frac{x_1 x_2 M_1 M_2}{(M_1 + M_2)^2} \left(\frac{55}{4} - 3B_{12}^* - 4A_{12}^* \right)$$

while

$$\lambda_{\text{mix}}^{\text{int}} = \frac{\lambda_1^{\text{int}}}{1 + \left(D_{11}^{\text{int}}/D_{12}^{\text{int}}\right) x_2/x_1} + \frac{\lambda_2^{\text{int}}}{1 + \left(D_{22}^{\text{int}}/D_{12}^{\text{int}}\right) x_1/x_2} \tag{6}$$

Here n is the total mole density, λ_i^{int} is defined as $\lambda_i^{\text{int}} = \lambda_i - \lambda_i^{\text{mon}}$, D_{12} is the mutual diffusion coefficient, and D_{11}^{int}, D_{22}^{int}, and D_{12}^{int} are coefficients of diffusion of internal energy. As an approximation, D_{11}^{int}, D_{22}^{int}, and D_{12}^{int} are usually replaced by the ordinary diffusion coefficients [6]. A_{12}^* and B_{12}^* are functions of the reduced temperature T_{12}^* as given by Hirschfelder et al. [7]. Now, as the only adaptable parameter, D_{12} can be found from the experimental results by a least square fit using D_{12} as fitting parameter. For the best fit, the difference between calculated and experimental λ values was found to be within 1% for the N_2–Freon 11 mixtures and within 0.5% for the N_2–Freon 12 mixtures (see Table I). It was found that for N_2–Freon 11 mixtures, $D_{12} = 7.73 \times 10^{-6}\ \text{m}^2 \cdot \text{s}^{-1}$, and for N_2–Freon 12 mixtures, $D_{12} = 9.23 \times 10^{-6}\ \text{m}^2 \cdot \text{s}^{-1}$, both at 101.3 kPa. These diffusion coefficients are estimated to be accurate within 2% for N_2–Freon 12 and within 4% for N_2–Freon 11, due to experimental accuracy. Because the values of A_{12}^* and B_{12}^* are calculated from a Lennard–Jones potential, an additional systematic error may be present.

Calculation of D_{12}, using Lennard–Jones parameters [7] ($\sigma_{12} = 4.65 \times 10^{-10}$ m and $\Omega_{12}^{(1,1)*} = 1.150$ for N_2–Freon 11 mixtures, and $\sigma_{12} = 4.51 \times 10^{-10}$ m and $\Omega_{12}^{(1,1)*} = 1.110$ for N_2–Freon 12 mixtures) yields $D_{12} = 7.71 \times 10^{-6}\ \text{m}^2 \cdot \text{s}^{-1}$ for N_2–Freon 11 and $D_{12} = 8.61 \times 10^{-6}\ \text{m}^2 \cdot \text{s}^{-1}$ for N_2–Freon 12, which is in good agreement with experiment. This is rather surprising, since the Lennard–Jones parameters are derived from the second virial coefficients of the pure gases, which are strongly influenced by dipole-dipole interaction. That is, the Lennard–Jones potential is a poor model for the polar Freons, so that the values of D_{12}, calculated from this model, are likely to be inaccurate. In contrast, the use of Eqs. (4)–(6) to obtain D_{12} from λ_{mix} is almost model independent. The model enters only through A_{12}^* and B_{12}^*, and a change of ± 10% in A_{12}^* and B_{12}^* is reflected as a change of ± 1.5% in D_{12}.

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