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Transport Properties of Freon-152a and Freon-142b in the Temperature Range of 280–510 K

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The thermal conductivity of 1,1 difluoroethane (Freon-152a) and 1 chloro-1 difluoroethane (Freon-142b) are measured at several pressures in the range 29.7–75.8 kPa and as a function of temperature in the range 280–510 K. The thermal conductivity column instrument is employed, and the experimental values are estimated to be accurate within a maximum uncertainty of ±5.6% at the lowest temperature, which reduces to ±2.4% at the highest temperature. These conductivity values are compared with the predictions of Chapman-Enskog kinetic theory, with the correction factor for the internal energy transport estimated from Hirschfelder's theory, and the Lennard-Jones (12-6) potential. The experimental conductivity data are also utilized to generate the values for the two other transport properties in conjunction with the interrelations obtained between different properties on the basis of kinetic theory. The data on transport properties are employed to give the best possible estimates of Prandtl and Schmidt numbers as a function of temperature.

KEY WORDS: thermal conductivity; transport properties; Freon-152a and Freon-142b; Prandtl and Schmidt numbers; kinetic theory.

1. INTRODUCTION

Freons, Genetrons, or Isotrons are different trade names commonly employed for various derivatives of methane and ethane in which the hydrogen atoms are replaced by fluorine and chlorine. These substances possess properties essential for practical refrigerants and are therefore of particular importance

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to scientists and engineers engaged in refrigeration technology. The difluoroethane group is characterized by successive replacement of hydrogen by chlorine with an unaltered number of fluorine atoms. Two members of this group are 1,1 difluoroethane (Freon-152a) and 1 chloro-1 difluoroethane (Freon-142b), for which no data on transport properties are available. We will refer to these refrigerants as F-152a and F-142b. It may be pointed out that the three digit numeral has the following significance [1]. Counting from right to left, the first digit represents the number of fluorine atoms in the compound, the second digit is one greater than the number of hydrogen atoms in the compound, and the third digit one less than the number of carbon atoms in the compound. The letter of the alphabet following the number is arbitrarily added to distinguish a compound from its isomers.

Here we report the thermal conductivity of F-152a and F-142b as measured on a conductivity column in the temperature range 280–510 K and at three pressures in the range where conductivity is found to be independent of pressure. These data are represented as polynomials in temperature and are employed to generate the two other transport properties, viz., viscosity and diffusion coefficients. This is done on the basis of interrelations among the different properties as derived from kinetic theory. The theoretical expressions for viscosity and diffusion coefficients are also employed to compute these properties in conjunction with Lennard-Jones (12-6) potential. The potential parameters are determined from semiempirical expressions involving critical constants. The contribution of internal degrees of freedom to the transport of internal energy is computed from the relatively simple theory of Hirschfelder [2]. Knowing the transport properties, the Prandtl and Schmidt numbers are computed for the two refrigerants as a function of temperature as an aid to engineering design calculations involving energy and mass transfer.

2. EXPERIMENTATION

The general design of the heat transfer conductivity column is the same as that of Chen and Saxena [3]; it has been used in this laboratory to determine a number of thermophysical properties of gases and metal wires [4]. The system is modified to enable the measurements to be taken below room temperature. This is accomplished by having a constant temperature bath with a circulator, operating at the melting point of ice. The maintenance of the column cold wall temperature near the ice point enables the conductivity measurements to be taken at as low a temperature as 280 K.

The column used in these experiments is 8 mm in diameter, and the tungsten wire is 0.3048 mm in diameter and 60 cm in length. The tungsten wire is annealed in a vacuum for about 4 h at 2400 K, and the heating is

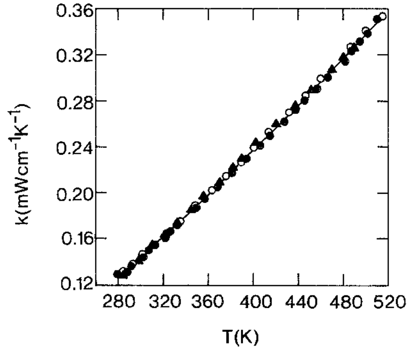

Fig. 1. Experimental thermal conductivity, k, values for Freon-152a as a function of temperature, T, at pressures of ● 29.7, ○ 53.5, and ▲ 75.8 kPa. The continuous line is a least-squares fit through all three data sets.

repeated for about 15 min before making a gas run. The measurements are performed on research grade pure Freon-152a and Freon-142b donated to us by Pennwalt Corporation. The tungsten wire is used as a resistance thermometer in addition to its function as a heater, and for this purpose it is calibrated at the triple point of water and at the freezing points of tin, cadmium, zinc, and aluminum as outlined by Jody and Saxena [5].

The heat transfer rate data for F-152a are taken at pressures of 29.7, 53.2, and 75.8 kPa. The preliminary calculations indicated that at such pressures the convected energy is negligibly small as compared to the conducted energy [3]. The calculated thermal conductivity values are plotted in Fig. 1 as a function of temperature at all three pressure levels. It is clear from the three sets of values that there is no systematic trend among them, and this confirms that the convection contribution is negligibly small as it is dependent on gas pressure. The three sets of data are corrected for the wall effect, the change in wire diameter due to the change in its length, and fluctuations in the cold wall temperature. All the data points are synthesized by the method of least squares and a quadratic polynomial in temperature. The following expression correlated the data within an average absolute and maximum deviations of 0.72 and 1.9%, respectively:

$$k(T) = -8.357 \times 10^{-2} + 6.320 \times 10^{-4}\,T + 4.257 \times 10^{-7}\,T^2 \qquad (1)$$

Here k represents the thermal conductivity coefficient, expressed in mW/cm K, and the temperature T is in degrees Kelvin. The continuous solid line in Fig. 1 is based on Eq. (1). The estimated maximum percentage errors in the experimental data points are ±5.0, ±3.2, and ±2.3% at 297, 395, and 509 K, respectively. In Fig. 2 the curves labeled "4" represent the maximum probable errors of our measurements. Also to be noted in this figure are the deviation plots of the three data sets from the predictions of Eq. (1). In each

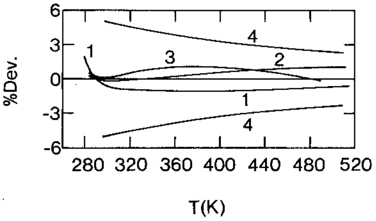

Fig. 2. Comparison of the individual data sets with the smoothed thermal conductivity values of Freon-152a. Curves 1, 2, and 3 refer to pressures of 29.7, 53.5, and 75.8 kPa, respectively. Curves 4 are computed error bands of conductivity data. % Dev. = [*k*(Eq. 1) − *k*(exptl.)] 100/*k*(Eq. 1).

case the actual data points scatter much less from the smoothed values in comparison to the experimental uncertainties of the experiments.

Similar measurements taken for F-142b at pressures of 30.9, 50.6, and 53.8 kPa are given in Fig. 3 as a function of temperature. The computed maximum percentage errors in the experimental data points are ±5.6, ±3.7, and ±2.9% at 297, 407, and 494 K, respectively, and the curves "4" of Fig. 4 represent these errors. The experimental data points are correlated by the following cubic polynomial in temperature and within an average absolute and maximum deviation of 1.5 and 4.2%, respectively:

$$k(T) = 0.1414 - 1.144 \times 10^{-3}\,T + 4.989 \times 10^{-6}\,T^2 - 4.358 \times 10^{-9}\,T^3 \qquad (2)$$

The continuous curve of Fig. 3 is based on Eq. (2). A careful study of Fig. 3 again suggests the contribution of the convection mode to the total heat transfer process as being negligible. Also to be noted in Fig. 4 is the fact that the scatter of the experimental values from the smoothed values of Eq. (2) is always less than the maximum probable errors of the measurement.

3. COMPARISON WITH THEORY: THERMAL CONDUCTIVITY

The kinetic theory of spherically symmetric monatomic gases undergoing elastic collisions is well understood [6]. However, the prediction of transport properties becomes increasingly difficult with the increasing

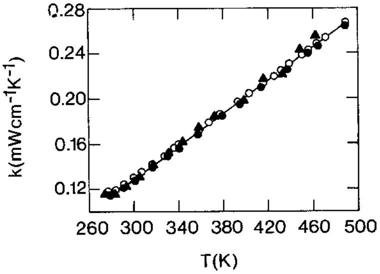

Fig. 3. Experimental thermal conductivity, *k*, values for Freon-142b as a function of temperature, *T*, at pressures of ● 30.9, ○ 50.6, and ▲ 53.8 kPa. The continuous line is a least-squares fit through all three data sets.

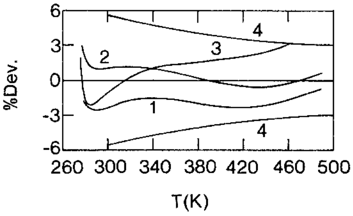

Fig. 4. Comparison of the individual data sets with the smooth thermal conductivity values of Freon-142b. Curves 1, 2, and 3 refer to pressures of 30.9, 50.6, and 53.8 kPa, respectively. Curves 4 are computed error bands of conductivity data. % Dev. = [k(Eq. 2) − k(exptl.)] 100/k(Eq. 2).

complexity in the molecular structure of a gas [7]. Many macroscopic and microscopic theories have been developed, sometimes on semiempirical grounds, to compute transport properties. Four of the theories for the coefficient of thermal conductivity are due to Hirschfelder [2], Mason and Monchick [8], Saxena et al. [9], and Ahtye [10]. Due to the lack of knowledge of the molecular constants of these two gases pertaining to energy transfer, only the theory of Hirschfelder will be considered here. According to this theory, the kinetic expression for the thermal conductivity coefficient is [2]

$$k = 0.8328 \frac{(T/M)^{1/2} f_k^{(3)}(T^*) f_E}{\sigma^2 \Omega^{(2,2)*}(T^*)} \tag{3}$$

Here the conductivity coefficient k is in mW/cm K, T is the temperature in K, M is the molecular weight of gas, $f_k^{(3)}$ is the third-order higher approximation correction factor and is a function of the reduced temperature $T^* = k_B T/\epsilon$, k_B is the Boltzmann constant, and ϵ is the depth of the intermolecular potential well, σ is the collision diameter in Å, $\Omega^{(2,2)*}$ is the reduced collision integral and is a function of the reduced temperature, and f_E is the Eucken-type correction factor. The value of f_E on Hirschfelder's molecular model is [2]

$$f_E = 0.115 + 0.354\,(C_p/R) \tag{4}$$

where C_p is the specific heat at constant pressure and R is the gas constant. $f_k^{(3)}$ and $\Omega^{(2,2)*}$ are tabulated as a function of T^* for various intermolecular potential parameters, and these are determined by matching experimental data with the theoretical values.

The potential parameters for both of these gases are not known, primarily because of the lack of experimental data on the coefficient of viscosity. We have therefore assumed the Lennard-Jones (12-6) potential as adequate for these two gases, with the potential parameters evaluated from the critical constant data and the following semiempirical relations [7, 11]:

$$\epsilon/k_B = 0.77\,T_C \tag{5}$$

Table I. The Lennard-Jones (12-6) Potential Parameters

Gas	ϵ/k_B (K)	σ (Å)
Freon-152a	298	4.76
Freon-142b	316	4.87

and

$$\sigma = 0.841\ v_c^{1/3} \tag{6}$$

where T_C is the critical temperature and v_c is the molar critical volume. The values of T_c and v_c for F-152a and F-142b are taken from ASHRAE handbook [12]. C_p data are also taken from ASHRAE handbook, which refers to 1.013×10^5 Pa in the case of F-152a, and for F-142b these are the limiting values for zero pressure. For F-142b, the σ value is obtained from Eq. (3) instead of Eq. (6). This involves matching the experimental k data at 380 and 400 K with those given by Eq. (3) with σ as the adjustable parameter. This yielded an average value of 4.87 ± 0.02 Å. Equation (6) leads to a value of 5.16 Å. The parameters are listed in Table I.

The computed values of conductivity from Eqs. (3) and (4) and the procedure outlined above are given in Tables II and III in column 3 for F-152a and F-142b, respectively, as a function of temperature. The experi-

Table II. Transport Properties of 1,1 Difluoroethane (Freon-152a)

	k (mW/cm K)	$\mu \times 10^4$ (Ns/m^2)			$D \times 10^1$ (cm^2/s)^a		Pr	Sc
T (K)	explt.	Eq. (3)	Eq. (9)	Eq. (7)	Eq. (10)	Eq. (8)	Eq. (11)	Eq. (12)
280	0.127	0.138	0.089	0.098	0.414	0.452	0.717	0.748
300	0.144	0.153	0.098	0.105	0.485	0.520	0.722	0.753
320	0.162	0.170	0.107	0.112	0.561	0.589	0.728	0.758
340	0.181	0.188	0.114	0.119	0.634	0.664	0.725	0.760
360	0.199	0.206	0.122	0.125	0.720	0.743	0.729	0.758
380	0.218	0.225	0.129	0.132	0.801	0.826	0.731	0.760
400	0.237	0.242	0.136	0.139	0.894	0.912	0.727	0.756
420	0.257	0.262	0.143	0.146	0.983	1.001	0.730	0.759
440	0.277	0.280	0.150	0.152	1.081	1.094	0.732	0.759
460	0.297	0.300	0.157	0.158	1.182	1.194	0.732	0.759
480	0.318	0.321	0.163	0.165	1.282	1.294	0.730	0.758
500	0.339	0.342	0.170	0.171	1.384	1.396	0.733	0.763
510	0.350	0.352	0.173	0.174	1.439	1.450	0.732	0.762

[a] These values correspond to a pressure of 1.013×10^5 Pa (1 atm).

Table III. Transport Properties of 1 Chloro-1 Difluoroethane (Freon-142b)

	k (mW/cm K)	$\mu \times 10^4$ (Ns/m^2)			$D \times 10^1$ (cm^2/s)^a		Pr	Sc
T(K)	exptl.	Eq. (3)	Eq. (9)	Eq. (7)	Eq. (10)	Eq. (8)	Eq. (11)	Eq. (12)
280	0.117	0.121	0.107	0.112	0.326	0.340	0.728	0.753
300	0.130	0.136	0.112	0.120	0.371	0.390	0.729	0.754
320	0.143	0.150	0.123	0.128	0.424	0.443	0.730	0.755
340	0.158	0.163	0.132	0.136	0.483	0.500	0.731	0.756
360	0.173	0.176	0.141	0.144	0.547	0.559	0.731	0.756
380	0.188	0.189	0.151	0.152	0.618	0.622	0.731	0.757
400	0.203	0.201	0.161	0.160	0.694	0.688	0.731	0.757
420	0.218	0.213	0.171	0.167	0.773	0.757	0.732	0.759
440	0.233	0.225	0.181	0.175	0.856	0.827	0.732	0.759
460	0.247	0.235	0.191	0.182	0.946	0.901	0.732	0.759
480	0.260	0.245	0.201	0.189	1.039	0.978	0.732	0.758
490	0.272	0.250	0.210	0.193	1.106	1.019	0.732	0.758

[a] These values correspond to a pressure of 1.013×10^5 Pa (1 atm).

mental values are also given in column 2 of these tables as obtained from Eq. (1) and (2). The agreement between the experiment and theory is only fair; the average absolute deviations for F-152a and F-142b for the entire temperature range are 3.0 and 3.8%, respectively. This highlights the importance of experimental measurements for these complicated molecules of importance to industry and the inadequacy of the theory to predict thermal conductivity with sufficient accuracy. The reason for the latter is believed to be due to a complicated unknown mechanism responsible for the transport of internal energy. In accordance with the earlier observation of Kessel'man et al. [13], made in connection with the thermal conductivity of liquid Freons of the ethane series, the thermal conductivity of F-142b is also smaller than that of F-152a, and this is attributed to the larger molecular weight of the former as compared to the latter. As pointed out above for F-142b, zero pressure C_p data are used. With increase in pressure, C_p will increase, and hence f_E and k will also.

4. PREDICTION OF VISCOSITY AND DIFFUSION COEFFICIENTS

The kinetic theory [6, 7] leads to the following expressions for the viscosity and diffusion coefficients of a gas:

$$\mu \times 10^6 = 2.6693 \frac{(MT)^{1/2} f_\mu^{(3)}(T^*)}{\sigma^2 \Omega^{(2,2)*}(T^*)} \tag{7}$$

$$D = 266.28 \frac{(T^3/M)^{1/2} f_D^{(2)}(T^*)}{P\sigma^2 \Omega^{(1,1)*}(T^*)} \tag{8}$$

Here μ is the coefficient of viscosity in N s/m^2, $f_\mu^{(3)}$ is the third-order correction factor for viscosity, D is the diffusion coefficient in cm^2/s, $f_D^{(2)}$ is the second-order correction factor for the diffusion coefficient, P is the gas pressure in Pa, and $\Omega^{(1,1)*}$ is the reduced collision integral. Computed values of μ and D for the Lennard-Jones (12-6) potential from Eqs. (7) and (8) as a function of temperature, with parameters given in Table I for these two gases, are recorded in Tables II and III. In the absence of experimental data, the values constitute a good base for establishing these properties. These calculations enjoy a great degree of confidence as the momentum and mass transport is known to be only weakly influenced by the internal degrees of freedom of a polyatomic molecule.

Many workers have estimated the values of one transport property by interconnecting its theoretical expression with that of another property whose experimental data are known. Such interrelations are quite reliable, as the explicit knowledge of the intermolecular potential is not implicit to the calculation scheme. The only requirement is that these must be central. Such relations involving elementary transport coefficients have been discussed by Saxena and Agrawal [14], Gandhi and Saxena [15], and Mathur and Saxena [16], among others. Equations (3) and (7) lead to the following expression for the interrelation between viscosity and conductivity under the assumption that $f_k^{(3)} = f_\mu^{(3)}$,

$$\mu = 3.205 \times 10^{-6} (kM/f_E) \tag{9}$$

Similarly, from Eqs. (3) and (8), we get

$$D = 319.7 \frac{\Omega^{(2,2)*}}{\Omega^{(1,1)*}} \frac{T f_D^{(2)}}{P f_k^{(3)}} \frac{k}{f_E} \tag{10}$$

Computed values of μ and D from Eqs. (9) and (10) on the basis of k data given in column 2 of Tables II and III are reported for the two gases in columns 4 and 6 of these tables. The reliability of these μ and D values is regarded as better than the values obtained on the basis of Eqs. (7) and (8).

In the calculations of heat and mass transfer two dimensionless numbers, viz., the Prandtl (Pr) and Schmidt (Sc) numbers, are required quite frequently. These are expressed in terms of the transport properties by the following relations:

$$\mathrm{Pr} = \mu C_p / k \tag{11}$$

$$\mathrm{Sc} = \mu/\rho D \qquad (12)$$

Calculated values of Pr and Sc numbers are given in Tables II and III for these two gases as a function of temperature. It may be noted that at least for the temperature range of the present investigations, both these numbers for both the gases are approximately constant, and they differ from each other by only a small amount, about 3%.

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