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Gaseous Thermal Conductivity of Difluoromethane (HFC-32), Pentafluoroethane (HFC-125), and Their Mixtures[1]

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The gaseous thermal conductivity of difluoromethane (HFC-32), pentafluoroethane (HFC-125), and their binary mixtures was measured with a transient hot-wire apparatus in the temperature ranges 283–333 K at pressures up to saturation. The uncertainty of the data is estimated to be within 1%. The thermal conductivity as a function of composition of the mixtures at constant pressure and temperature is found to have a small maximum near 0.3–0.4 mole fraction of HFC-32. The gaseous thermal-conductivity data obtained for pure HFC-32 and HFC-125 were correlated with temperature and density together with the liquid thermal-conductivity data from the literature, based on the excess thermal-conductivity concept. The composition dependence of the thermal conductivity at a constant temperature is represented with the aid of the Wassiljewa equation.

KEY WORDS: difluoromethane; hydrofluorocarbon; HFC-32; HFC-125; pentafluoroethane; refrigerant; thermal conductivity; transient hot-wire method.

1. INTRODUCTION

The binary refrigerant mixture consisting of HFC-32 (difluoromethane; CH_2F_2) and HFC-125 (pentafluoroethane; CHF_2–CF_3) is expected to be one of the most favorable alternatives to the working fluid HCFC-22 (monochlorodifluoromethane; $CHClF_2$) in refrigeration, heat pumps, and air-conditioning. Few accurate measurements of the thermal conductivity of gaseous mixtures exist. As a continuation of the study of the thermophysical

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properties of environmentally acceptable alternative refrigerants, this paper reports thermal-conductivity data for gaseous (HFC-32 + HFC-125) mixtures.

2. EXPERIMENTS

Thermal conductivity was measured with a transient hot-wire apparatus. The apparatus and procedure have been described in detail in a previous publication [1]. For the heat source, two platinum wires 5 μm in diameter and 50 and 25 mm in length were used to compensate for end effects. As a check of the operation of the instrument, nitrogen and argon were measured before and after the sample fluids. The values obtained for these gases were in good agreement with the reference values [2, 3]. HFC-32 was supplied by Showa Denko Co., Ltd. and was 99.99 mol% pure. HFC-125 was from Daikin Industries, Ltd., and had a purity of 99.8 mol%. These fluids were used without further purification. The mixtures were prepared gravimetically and the uncertainty in the composition was less than 0.6 mol%. The uncertainty in the experimental data is estimated to be within 1%.

3. RESULTS AND CORRELATIONS

In Tables I, II, and III the experimental results for HFC-32, HFC-125, and their binary mixtures are presented. The densities of HFC-32 and HFC-125 were obtained from the equations of state of Piao et al. [4] and Wilson et al. [5], respectively.

3.1. Thermal Conductivity of Pure Components

3.1.1. Thermal Conductivity at Atmospheric Pressure

The gaseous thermal conductivity of HFC-32 and HFC-125 at atmospheric pressure increases almost linearly with increasing temperature. The thermal conductivity of the pure components at atmospheric pressure $\lambda_0(T)$ as a function of the temperature T is represented by a polynomial:

$$\text{HFC-32:} \qquad \lambda_0(T) = 2.706 \times 10^{-3}T + 1.2578 \times 10^{-4}T^2 \qquad (1)$$

$$\text{HFC-125:} \qquad \lambda_0(T) = 1.507 \times 10^{-2}T + 1.001 \times 10^{-4}T^2 \qquad (2)$$

where λ_0 is in $\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ and T in K. The validity of these equations is for the range 283 to 333 K.

Table I. Thermal Conductivity of Gaseous HFC-32

P (MPa)	ρ (kg·m^{-3})[a]	λ (mW·m^{-1}·K^{-1})
	283.15 K	
0.10	2.243	10.84
0.20	4.555	10.95
0.30	6.942	11.09
0.40	9.411	11.27
0.50	11.97	11.45
0.60	14.63	11.67
0.70	17.39	11.89
0.80	20.28	12.16
0.90	23.30	12.43
1.00	26.47	12.77
1.05	28.12	12.93
1.11	30.06	13.12
	298.15 K	
0.10	2.124	11.99
0.20	4.303	11.99
0.30	6.539	12.14
0.50	11.20	12.40
0.70	16.14	12.75
0.90	21.42	13.12
1.00	24.20	13.29
1.10	27.09	13.55
1.20	30.10	13.86
1.30	33.24	14.12
1.50	39.98	14.75
1.62	44.38	15.21
1.69	47.10	15.44
	313.15 K	
0.10	2.019	13.20
0.30	6.186	13.40
0.51	10.77	13.62
0.70	15.11	13.83
0.91	20.16	14.14
1.10	24.99	14.38
1.30	30.39	14.97
1.50	36.15	15.44
1.73	43.31	15.96
1.83	46.64	16.10
2.00	52.66	16.65
2.21	60.84	17.57
2.33	65.98	18.15
2.48	72.87	18.58

[a] Calculated from the equation of state by Piao et al. [4].

Table I. (*Continued*)

P (MPa)	ρ (kg·m^{-3})[a]	λ (mW·m^{-1}·K^{-1})
	333.15 K	
0.10	1.894	14.85
0.30	5.776	14.97
0.51	10.00	15.19
0.70	13.97	15.42
1.01	20.75	15.68
1.27	26.80	15.89
1.51	32.69	16.42
1.71	37.88	16.85
2.01	46.19	17.49
2.31	55.27	18.28
2.62	65.66	19.11
3.00	80.29	20.25
3.46	102.3	21.72
3.93	134.8	23.54

Table II. Thermal Conductivity of Gaseous HFC-125

P (MPa)	ρ (kg·m^{-3})[a]	λ (mW·m^{-1}·K^{-1})
	283.15 K	
0.10	5.190	12.29
0.20	10.58	12.35
0.30	16.18	12.41
0.40	22.02	12.51
0.50	28.14	12.62
0.60	34.56	12.74
0.70	41.34	12.90
0.80	48.53	13.08
0.85	52.30	13.19
0.91	56.92	13.30
	298.15 K	
0.10	4.914	13.41
0.20	9.980	13.46
0.30	15.21	13.51
0.40	20.62	13.60
0.50	26.23	13.72

[a] Calculated from the equation of state by Wilson et al. [5].

Table II. (*Continued*)

P (MPa)	ρ $(kg \cdot m^{-3})^a$	λ $(mW \cdot m^{-1} \cdot K^{-1})$
0.60	32.06	13.83
0.70	38.13	14.05
0.80	44.48	14.07
0.90	51.12	14.25
1.00	58.12	14.39
1.10	65.51	14.67
1.20	73.38	14.79
1.30	81.80	15.10
1.38	88.84	15.24
	313.15 K	
0.10	4.667	14.51
0.20	9.455	14.60
0.30	14.37	14.74
0.50	24.63	14.92
0.70	35.53	15.11
0.90	47.19	15.26
1.10	59.77	15.52
1.20	66.47	15.72
1.30	73.48	15.98
1.40	80.86	16.20
1.50	88.64	16.33
1.60	96.90	16.61
1.70	105.7	16.90
1.80	115.2	17.18
2.01	138.0	17.72
	333.15 K	
0.10	4.376	16.06
0.20	8.842	16.03
0.30	13.40	16.14
0.40	18.06	16.21
0.50	22.83	16.29
0.60	27.70	16.32
0.70	32.70	16.39
0.80	37.82	16.52
0.90	43.07	16.60
1.00	48.47	16.66
1.20	59.74	16.84
1.40	71.72	17.21

Table III. Thermal Conductivity of Gaseous (HFC-32 + HFC-125) Mixtures

x^a	P (MPa)	λ ($\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)
	283.15 K	
0.1876	0.10	12.41
	0.20	12.44
	0.30	12.53
	0.40	12.61
	0.50	12.72
	0.60	12.83
0.3696	0.10	12.46
	0.20	12.51
	0.30	12.58
	0.40	12.71
	0.50	12.84
	0.60	13.06
	0.70	13.26
0.5721	0.10	12.26
	0.20	12.31
	0.30	12.43
	0.40	12.62
	0.50	12.80
	0.60	13.00
	0.70	13.21
	0.76	13.35
0.8222	0.10	11.70
	0.20	11.79
	0.30	11.89
	0.40	12.04
	0.50	12.23
	0.60	12.48
	0.70	12.71
	0.80	13.02
	298.15 K	
0.1876	0.10	13.56
	0.20	13.61
	0.30	13.66
	0.40	13.74
	0.50	13.78
	0.65	13.95
	0.80	14.15
	0.90	14.31
	1.00	14.52
	1.08	14.67

[a] Mole fraction of HFC-32.

Table III. (*Continued*)

x^a	P (MPa)	λ ($mW \cdot m^{-1} \cdot K^{-1}$)
0.3730	0.10	13.59
	0.20	13.62
	0.30	13.68
	0.50	13.83
	0.70	14.06
	0.80	14.21
	0.90	14.39
	1.00	14.57
	1.20	15.02
0.6129	0.10	13.31
	0.20	13.38
	0.30	13.46
	0.50	13.64
	0.70	13.90
	0.80	14.05
	0.90	14.23
	1.00	14.43
	1.10	14.67
	1.20	14.95
0.8134	0.10	12.93
	0.20	12.96
	0.30	13.02
	0.40	13.09
	0.50	13.23
	0.60	13.36
	0.70	13.50
	0.80	13.67
	0.90	13.85
	1.00	14.09
	1.10	14.31

The thermal conductivities of HFC-32 and HFC-125 are larger than those of HCFC-22 at the same temperature by about 15 and 29%, respectively. The temperature coefficients of λ, $(\partial\lambda/\partial T)_p$, for both refrigerants are slightly larger than for HCFC-22.

3.1.2. *Thermal Conductivity at High Pressures*

The thermal conductivities of the pure components and their binary mixtures at 298.15 K are plotted as a function of pressure in Fig. 1. The thermal conductivity at constant temperature and constant composition

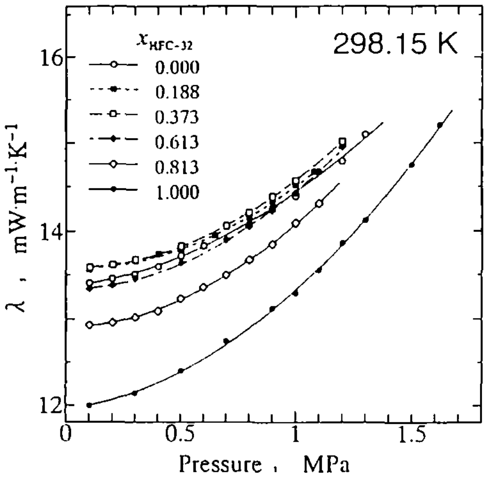

Fig. 1. Pressure and composition dependences of the thermal conductivity of the (HFC-32 + HFC-125) mixture at 298.15 K.

increases monotonically with increasing pressure up to the saturation pressure and exhibits a small positive curvature.

According to the excess transport-property concept, the thermal conductivity $\lambda(\rho, T)$ of a pure fluid at density ρ and temperature T may be considered as composed of three contributions, as follows:

$$\lambda(\rho, T) = \lambda_0(T) + \Delta\lambda_{ex}(\rho) + \Delta\lambda_c(\rho, T) \tag{3}$$

where $\lambda_0(T)$ is a dilute-gas term which depends on temperature only, $\Delta\lambda_{ex}(\rho)$ is an excess term (residual term) which accounts for the density (or pressure) dependence, and $\Delta\lambda_c(\rho, T)$ is a contribution which represents the critical enhancement. This equation can be used to correlate and calculate the three-dimensional surfaces of the thermal conductivity in the temperature-pressure plane. For HFC-32 and HFC-125 no experimental data are available at present close to the critical point in literature. Therefore, only the background thermal conductivity $\bar{\lambda}(\rho, T)$ has been tentatively determined in this work, based on the present experimental results in the gas phase together with the liquid thermal-conductivity data cited from Yata et al. [6] and from Papadaki and Wakeham [7].

$$\bar{\lambda}(\rho, T) = \lambda_0(T) + \Delta\lambda_{ex}(\rho) \tag{4}$$

$$\Delta\lambda_{ex}(\rho) = a_1\rho + a_2\rho^2 + a_3\rho^3 + a_4\rho^4 \tag{5}$$

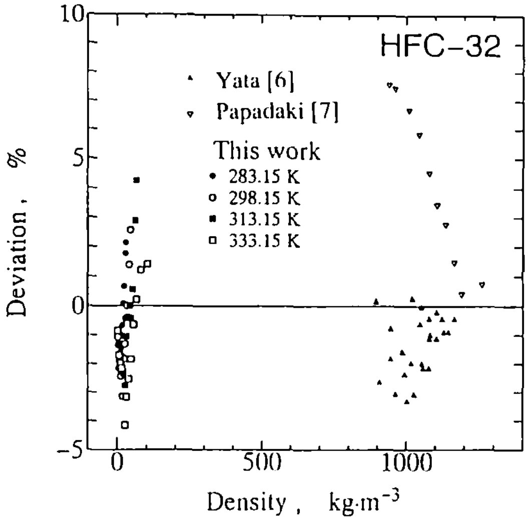

Fig. 2. Deviation plot of the present experimental results together with liquid thermal-conductivity data cited from the literature for HFC-32.

where $\Delta\lambda_{ex}$ is in mW · m^{-1} · K^{-1} and ρ in kg · m^{-3}. The coefficients in Eq. (5) for HFC-32 and HFC-125 are listed in Table IV. The validity of this equation is $\rho < 1250$ kg m^{-3} for HFC-32 and $\rho < 1500$ kg m^{-3} for HFC-125. It is found that Eqs. (4) and (5) represent our data and available literature values with a mean deviation of 4% for HFC-32 and 2% for HFC-125, respectively. The deviation plot of the experimental data used in this correlation for HFC-32 is shown in Fig. 2.

3.2. Thermal Conductivity of Binary Mixtures

The composition dependence of the thermal conductivity of (HFC-32 + HFC-125) mixtures at 283.15 and 298.15 K and various

Table IV. Coefficients in Eq. (5)

	HFC-32	HFC-125
a_1	6.4446×10^{-2}	1.4366×10^{-2}
a_2	-1.0430×10^{-5}	6.3141×10^{-5}
a_3	7.2038×10^{-8}	-8.2186×10^{-8}
a_4	-4.956×10^{-12}	3.8889×10^{-11}

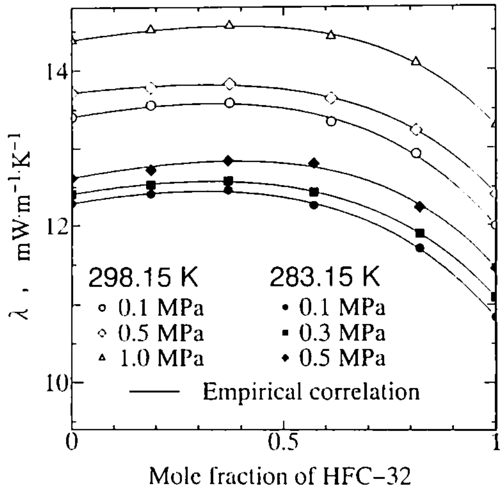

Fig. 3. Composition dependences of the thermal conductivity of (HFC-32 + HFC-125) mixture at 283.15 and 298.15 K at various pressures.

pressures is shown in Fig. 3. In this system, each isobar has a slight maximum near the mole fraction of HFC-32 $x = 0.3$–0.4. The composition where the maximum exists shifts gradually to a higher concentration of HFC-32 with increasing pressure.

Near ambient pressure, the composition dependence of the thermal conductivity of binary gaseous mixtures at a constant temperature can be expressed by the Wassiljewa equation [8].

$$\lambda_{0\,\mathrm{m}} = \frac{\lambda_{0\,1}}{1 + A_{1\,2}(x_2/x_1)} + \frac{\lambda_{0\,2}}{1 + A_{2\,1}(x_1/x_2)} \qquad (6)$$

where $\lambda_{0\,\mathrm{m}}$ and $\lambda_{0\,i}$ are the thermal conductivities of mixture and pure component i, respectively, x_i is the mole fraction, and A_{ij} is the combination factor characteristic to the mixture and temperature. The thermal conductivity of a mixture at any composition can be calculated from this equation based on the values of pure components, if the combination factors A_{ij} are known. The actual values of A_{ij} are determined from a fit to the experimental data for the mixtures. The values thus obtained for A_{ij} are listed in Table V together with the maximum and mean deviations of the experimental data from Eq. (6). Generally, the Wassiljewa equation is valid for dilute gaseous mixtures near ambient pressure. However, it is found in this work that the equation is appropriate up to 1 MPa for (HFC-32 + HFC-125) mixtures.

Table V. Optimum Values of the Combination Factors in Eq. (6)

Temperature (K)	Pressure (MPa)	A_{12}	A_{21}	Deviation (%)	
				Maximum	Average
283.15	0.10	1.286	0.612	0.19	0.13
	0.30	1.309	0.611	0.09	0.06
	0.50	1.413	0.565	0.40	0.26
298.15	0.10	1.370	0.586	0.34	0.21
	0.50	1.567	0.537	0.14	0.09
	1.00	1.542	0.546	0.15	0.09

4. CONCLUSIONS

New measurements of the gaseous thermal conductivity of (HFC-32 + HFC-125) mixtures are reported. The measurements were performed in a transient hot-wire apparatus in the temperature range of 283–333 K at pressures up to saturation, with an uncertainty of ±1%.

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