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Equations for Thermal Conductivity of Natural Refrigerants[1]

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Experimental results for the thermal conductivity of ammonia, propane, butane, isobutane, and propylene are reviewed, with special attention given to the liquid phase. New equations for the thermal conductivity of these five substances applicable for practical use over wide ranges of temperature and pressure including the critical region are proposed based on the experimental data. The present equations as well as the existing equations are compared with the experimental data. Compared with existing equations for ammonia, isobutane, and propylene, which are not reliable in the liquid phase, the behavior of the thermal conductivity for these substances is much improved using the present equations.

KEY WORDS: ammonia; butane; correlating equation; isobutane; natural refrigerants; propane; propylene; thermal conductivity.

1. INTRODUCTION

As natural refrigerants have very low global warming potentials, they are candidates as refrigerants that will be used in the future. Despite the long history of the study of natural refrigerants, knowledge of the thermophysical properties is not complete, especially for the transport properties.

In this paper, the available experimental data and correlating equations of the thermal conductivity of ammonia, propane, butane, isobutane, and propylene are reviewed, with special focus on the liquid phase. New equations for the thermal conductivity of the five substances applicable over wide ranges of temperature and pressure are proposed.

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2. AVAILABLE EXPERIMENTAL DATA

The main purpose of the present paper is to correlate the thermal conductivity of natural refrigerants in the liquid phase. Thus, correlation of the thermal conductivity in the gaseous phase is not considered here. Instead existing correlations of the thermal conductivity in the gaseous phase at low pressures are used. In the present study only the experimental data on thermal conductivity at higher densities are considered.

The data sets [1–15] of the thermal conductivity of the five substances considered in the present correlation are summarized in Table I. The data sets were selected from the MIDAS Database [16], which compiles bibliographic references on thermophysical properties of numerous refrigerants. It seems

Table I. Experimental Data Sets for the Thermal Conductivity of Natural Refrigerants

First author	Phase[a]	Method[b]	Range	No. data	Year	Ref. No.
			Ammonia			
Golubev	LVC	C.C.	206–674 K, 0.1–40 MPa	218	1964	1
Needham	LVC	C.C.	294–450 K, 0.1–48 MPa	115	1965	2
Tufeu	LVC	C.C.	388–578 K, 1–80 MPa	122	1984	3
Clifford	L	C.C.	298–387 K, 1–51 MPa	40	1988	4
			Propane			
Roder	L	T.H.W.	112–299 K, 2–68 MPa	70	1982	5
Tufeu	LVC	C.C.	298–578 K, 1–70 MPa	175	1987	6
Prasad	LV	T.H.W.	193–322 K, 0.2–71 MPa	128	1989	7
Yata	L	T.H.W.	254–316 K, 1.2–30 MPa	16	1996	8
			Butane			
Kandiyoti	L	T.H.W.	148–252 K, 0.1 MPa	9	1972	9
Nieto de Castro	LVC	C.C.	298–601 K, 1–70 MPa	177	1983	10
Yata	L	T.H.W.	258–336 K, 0.5–20 Kpa	15	1996	8
			Isobutane			
Kazaryan	LVC	C.C.	193–414 K, 0.1–51 MPa	132	1969	11
Nieuwoudt	LVC	C.C.	293–630 K, 0.1–106 MPa	260	1987	12
Yata	L	T.H.W.	256–335 K, 1–15 MPa	20	1999	13
			Propylene			
Naziev	LV	C.C.	273–623 K, 0.1–50 MPa	140	1975	14
Swift	L	T.H.W.	280–340 K, 1–9 MPa	46	1984	15
Yata	L	T.H.W.	257–295 K, 1–15 MPa	12	1999	13

[a] L, liquid phase; V, gaseous phase; C, critical region.

[b] C.C., coaxial cylinder method; T.H.W., transient hot-wire method.

that the number of data sets for each substance is very low. But the authors are confident that Table I contains all comprehensive data sets for each substance published up to now.

3. EQUATIONS

The equation for the thermal conductivity λ of hydrocarbons as a function of temperature T and density ρ is

$$\lambda(T, \rho) = \lambda_0(T) + \Delta\lambda(\rho) + \Delta\lambda_c(T, \rho) \tag{1}$$

and the equation for ammonia is

$$\lambda(T, \rho) = \lambda_0(T) + \Delta\lambda(\rho) + \Delta\lambda_c(T, \rho) + \Delta\lambda_L(T, \rho) \tag{2}$$

where λ_0 denotes the ideal-gas thermal conductivity and is a function of temperature only. $\lambda - \lambda_0$ denotes the excess thermal conductivity, and at high temperatures it reduces to $\Delta\lambda(\rho)$, which is a function of density only. $\Delta\lambda_c$ denotes the critical enhancement of thermal conductivity and is significant only in the critical region. $\Delta\lambda_L$ is significant for ammonia only in its liquid phase.

The term λ_0 is expressed as follows:

$$\lambda_0(T) = a_0 + a_1(T/T_c) + a_2(T/T_c)^2 + a_3(T/T_c)^3 \tag{3}$$

where T_c denotes the critical temperature. As mentioned earlier, the term λ_0 is not correlated from the original data in this study. For ammonia and propylene the values tabulated by Krauss [17] and by Vargaftik [18], respectively, are used for fitting with Eq. (3). The values tabulated by Younglove and Ely [19] are used for propane, butane, and isobutane. The numerical values of the coefficients in Eq. (3) thus determined are given in Table II.

Outside the critical region the excess thermal conductivity $\lambda - \lambda_0$ of a fluid is usually expressed by a very simple function of density over a wide range of temperature and density. In Figs. 1–5, the values of the excess thermal conductivity for ammonia, propane, butane, isobutane, and propylene from the data sources listed in Table I are shown as a function of density. The values of density are calculated by the equations of state [19–21] contained in REFPROP Version 6.01 [22]. As discussed in our previous paper [13], the values for the excess thermal conductivity for isobutane of Kazaryan and Ryabtsev [11], in Fig. 4, and the values for propylene of Naziev [13], in Fig. 5, seem to be too large compared with the other sets of data in the liquid phase, namely, in the density region

Table II. Numerical Values of Coefficients in Equations for Thermal Conductivity

	Ammonia	Propane	Butane	Isobutane	Propylene
T_C (K)	405.4	369.9	425.2	407.9	365.9
P_C (MPa)	11.33	4.25	3.80	3.64	4.67
ρ_C ($kg \cdot m^{-3}$)	225.0	220.5	227.8	224.4	223.4
a_0 ($mW \cdot m^{-1} \cdot K^{-1}$)	−4.8016	4.4494	5.1626	4.3622	−2.3789
a_1 ($mW \cdot m^{-1} \cdot K^{-1}$)	27.210	−12.623	−18.552	−15.846	2.8167
a_2 ($mW \cdot m^{-1} \cdot K^{-1}$)	18.539	42.721	57.527	51.219	29.632
a_3 ($mW \cdot m^{-1} \cdot K^{-1}$)	−2.9257	−8.0681	−12.252	−10.752	−5.5098
b_1 ($mW \cdot m^{-1} \cdot K^{-1}$)	37.271	2.6645	8.8824	8.5804	13.652
b_2 ($mW \cdot m^{-1} \cdot K^{-1}$)	43.079	20.577	5.1298	7.4546	9.4265
b_3 ($mW \cdot m^{-1} \cdot K^{-1}$)	−5.7446	−9.3882	−1.1271	−5.1351	−2.2023
b_4 ($mW \cdot m^{-1} \cdot K^{-1}$)	3.5873	2.8979	1.3231	2.3399	1.2300
d_1 ($mW \cdot m^{-1} \cdot K^{-1}$)	−750.0				
d_2 ($mW \cdot m^{-1} \cdot K^{-1}$)	−4.5				
d_3 ($mW \cdot m^{-1} \cdot K^{-1}$)	−6.0				
Γ	0.063	0.056	0.053	0.058	
ξ_0 (nm)	0.15	0.20	0.21	0.23	
$(\bar{q}_D)^{-1}$ (nm)	0.28	0.50	0.55	0.65	

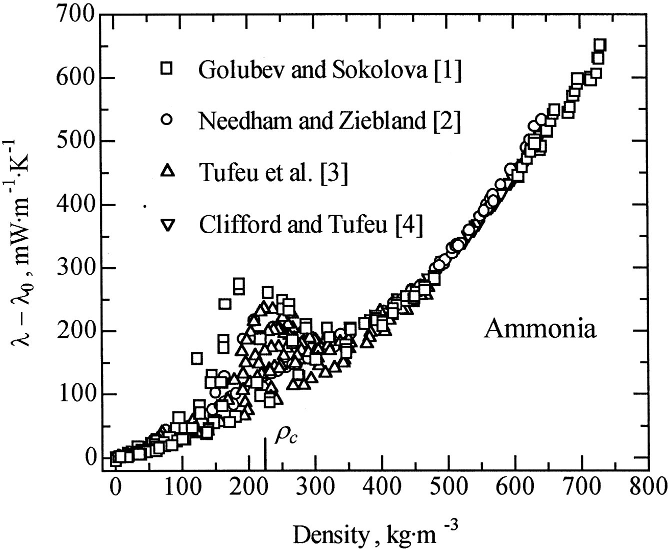

Fig. 1. Excess thermal conductivity of ammonia as a function of density.

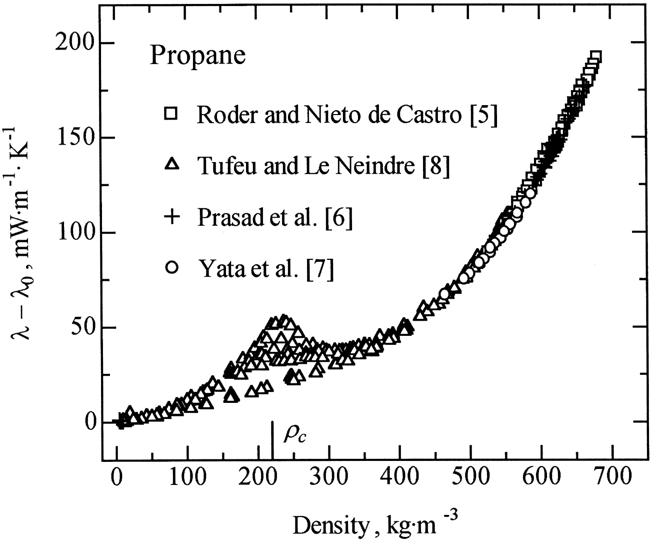

Fig. 2. Excess thermal conductivity of propane as a function of density.

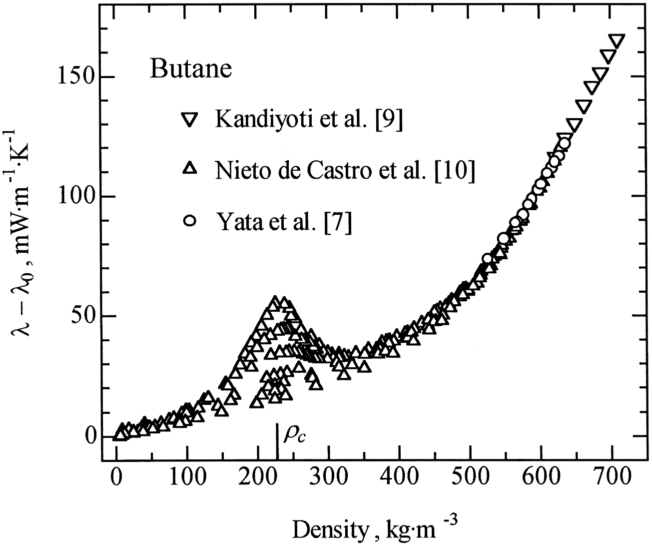

Fig. 3. Excess thermal conductivity of butane as a function of density.

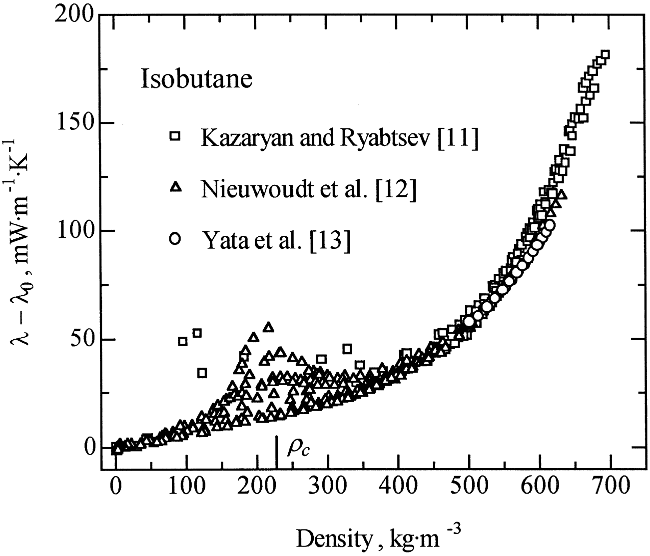

Fig. 4. Excess thermal conductivity of isobutane as a function of density.

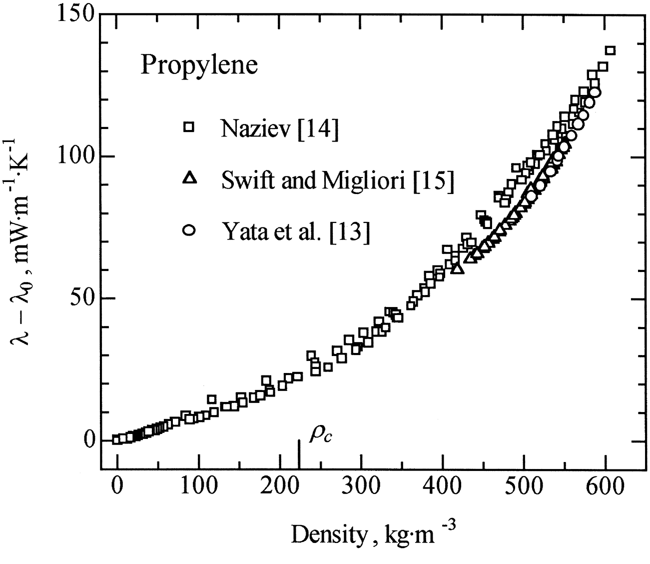

Fig. 5. Excess thermal conductivity of propylene as a function of density.

higher than 500 $\mathrm{kg \cdot m^{-3}}$. For propane (Fig. 2) and butane (Fig. 3) the values for the excess thermal conductivity of the different data sets agree well in the liquid phase.

Figures 1–4 include values in the critical region, namely, in the density range from 100 to 300 $\mathrm{kg \cdot m^{-3}}$ and near the critical temperature, and the behavior of the excess thermal conductivity is rather complicated. But if the values in the critical region are excluded, $\lambda - \lambda_0$ tends to $\Delta\lambda(\rho)$ for hydrocarbons. For ammonia an additional term, $\Delta\lambda_{\mathrm{L}}(T, \rho)$ is necessary. The terms $\Delta\lambda$ and $\Delta\lambda_{\mathrm{L}}$ are expressed as

$$\Delta\lambda(\rho) = b_1(\rho/\rho_{\mathrm{c}}) + b_2(\rho/\rho_{\mathrm{c}})^2 + b_3(\rho/\rho_{\mathrm{c}})^3 + b_4(\rho/\rho_{\mathrm{c}})^4 \tag{4}$$

$$\Delta\lambda_{\mathrm{L}}(T, \rho) = d_1 \exp\{d_2(T/T_{\mathrm{c}})^{1.5} + d_3(\rho/\rho_{\mathrm{c}})^{-5}\} \tag{5}$$

where ρ_{c} denotes the critical density. The numerical values of the coefficients determined by fitting experimental data with Eqs. (4) and (5) are listed in Table II.

Finally, to express the critical enhancement of the thermal conductivity, the term $\Delta\lambda_{\mathrm{c}}$ is necessary. As for the critical enhancement of thermal conductivity, many works have been published by Sengers and his coworkers [23, 24]. In this study the approximate treatment of Olchowy and Sengers [25] is adopted. They give an approximate equation for $\Delta\lambda_{\mathrm{c}}$ by using the critical enhancement of the thermal diffusivity ΔD_{T} as follows:

$$\Delta\lambda_{\mathrm{c}}(T, \rho) = \rho C_{\mathrm{p}} \Delta D_{\mathrm{T}} \tag{6}$$

ΔD_{T} is expressed as

$$\Delta D_{\mathrm{T}}(T, \rho) = \frac{R_0 k T}{6\pi\eta\xi}(\tilde{\Omega} - \tilde{\Omega}_0) \tag{7}$$

where

$$\tilde{\Omega} = \frac{2}{\pi}\left[\left(\frac{C_{\mathrm{p}} - C_{\mathrm{v}}}{C_{\mathrm{p}}}\right)\tan^{-1}(\bar{q}_{\mathrm{D}}\xi) + \frac{C_{\mathrm{v}}}{C_{\mathrm{p}}}\bar{q}_{\mathrm{D}}\xi\right] \tag{8}$$

$$\tilde{\Omega}_0 = \frac{2}{\pi}\left\{1 - \exp\left[\frac{-1}{(\bar{q}_{\mathrm{D}}\xi)^{-1} + (\frac{1}{3})(\bar{q}_{\mathrm{D}}\xi\rho_{\mathrm{c}}/\rho)^{-1}}\right]\right\} \tag{9}$$

$$\xi = \xi_0(\Delta\tilde{\chi}/\Gamma)^{\nu/\gamma} \tag{10}$$

$$\Delta\tilde{\chi} = \tilde{\chi}(T, \rho) - \tilde{\chi}(T_{\mathrm{R}}, \rho)\, T_{\mathrm{R}}/T \tag{11}$$

$$\tilde{\chi}(T, \rho) = \frac{P_{\mathrm{c}}\rho}{\rho_{\mathrm{c}}^2}\left(\frac{\partial\rho}{\partial P}\right)_T \tag{12}$$

In the equations above C_p, C_v, and η denote the specific heat capacity at constant pressure, the specific heat capacity at constant volume, and the viscosity, respectively. T_R is the reference temperature ($= 2.0T_c$ for propane, $= 1.5T_c$ for other substances) and k is the Boltzmann constant. R_0 ($= 1.01$) is a system-independent universal constant and ν ($= 0.63$) and γ ($= 1.239$) are the system independent universal exponents. Γ and ξ_0 are the system-dependent constants and are determined from the equation of state for each substance [19, 20] by the method described in Ref. 26. The cutoff parameter $\bar{q}_D$ for each substance is determined using the experimental data in the critical region. The values of $\bar{q}_D$ determined for the four substances except propylene are listed in Table II with the values of constants. As no experimental data in the critical region are available for propylene, the term $\Delta\lambda_c$ is not determined for this substance.

4. COMPARISONS WITH EXPERIMENTAL DATA

Comparisons of the experimental data for the thermal conductivity λ_{exp} with calculated values λ_{cal} are given in Figs. 6–10.

4.1. Ammonia

Figure 6 shows comparisons of the present equation for ammonia with experimental data sets [1–4]. The average deviation of the experimental data from the equation is 2.9%. The average deviation from the equation of Tufeu et al. [3] which is used in REFPROP [22] is 5.0%. The equation of Tufeu et al. does not seem to be suitable for the liquid phase.

4.2. Propane

Figure 7 shows comparisons of the present equation for propane with experimental data sets [5–8]. The average deviation of the experimental data from the equation is 1.9%. The average deviation of these data from the equation of Younglove and Ely [19] which is used in REFPROP [22] is 2.5%. The present equation as well as the one in REFPROP describe well the behavior of the thermal conductivity of propane.

4.3. Butane

Figure 8 shows comparisons of the present equation for butane with experimental data sets [8–10]. The average deviation of the experimental

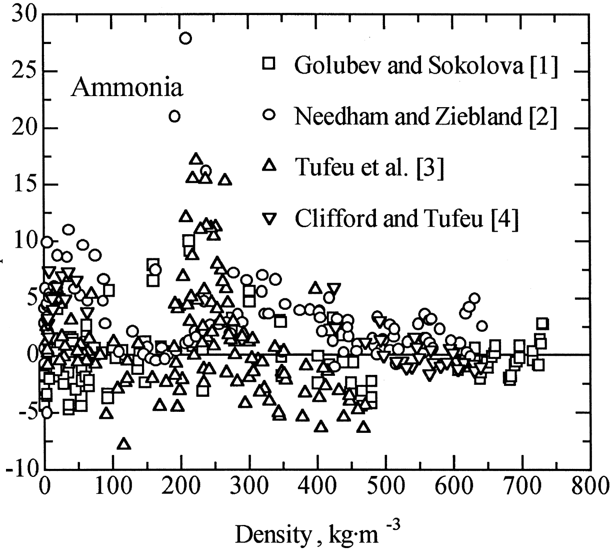

Fig. 6. Deviations of experimental data of the thermal conductivity of ammonia from the present model.

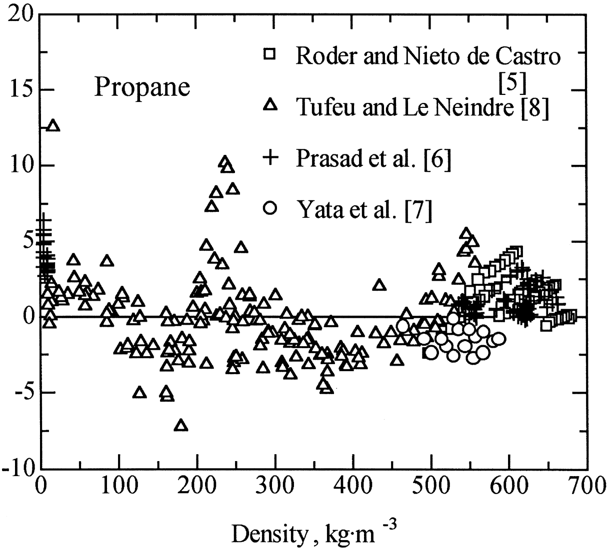

Fig. 7. Deviations of experimental data of the thermal conductivity of propane from the present model.

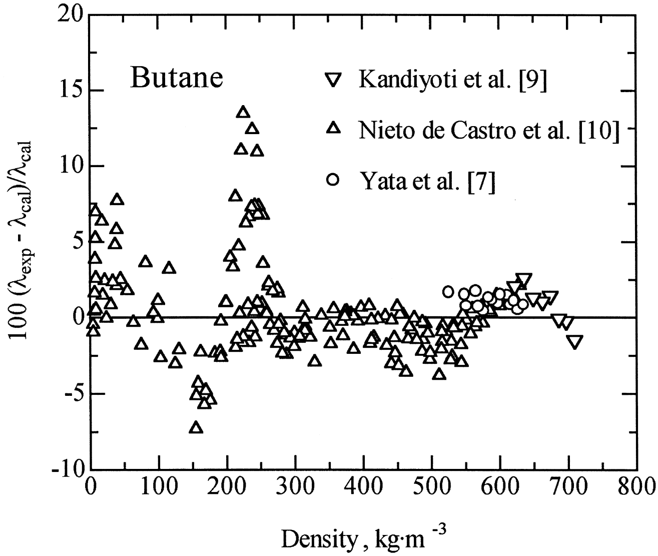

Fig. 8. Deviations of experimental data of the thermal conductivity of butane from the present model.

data from the equation is 2.0%. The average deviation from the equation of Younglove and Ely [19] which is used in REFPROP [22] is 2.6%. The present equation as well as the one in REFPROP describe well the behavior of the thermal conductivity of butane.

4.4. Isobutane

Figure 9 shows comparisons of the present equation for isobutane with experimental data sets [11–13]. The experimental data sets are also compared with the equation of Younglove and Ely which is contained in REFPROP [22]. As stated earlier, the data by Kazaryan and Ryabtsev have a different tendency from other sets of data and are estimated to be less accurate. The average deviations of the data of Kazaryan and Ryabtsev from both equations are almost the same and are as large as 8%. The average deviations of the data of Nieuwoudt et al. from the present equation and from the equation of Younglove and Ely are 2.2 and 3.6%, respectively. The deviations of the data of Yata et al. from the present equation and from that of Younglove and Ely are 2.6 and 6.0%, respectively. The equation of Younglove and Ely does not seem to agree well with reliable data sets [12, 13] in the liquid phase.

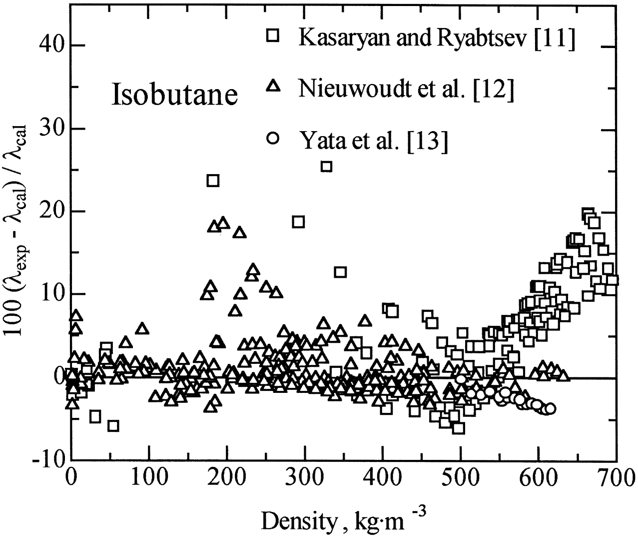

Fig. 9. Deviations of experimental data of the thermal conductivity of isobutane from the present model.

4.5. Propylene

Figure 10 shows the comparison of the present equation for propylene with experimental data sets [13–15]. The average deviation of the experimental data from the equation is 2.7%. That from the predictive ECS model of Huber et al. [27] which is used in REFPROP [22] is 6.7%. The values predicted by the equation of Huber et al. show large deviations from the reliable data sets [13, 15] in the liquid phase and do not seem to be the most appropriate.

4.6. Validity Ranges and Reliability of the Present Equations

From comparisons with the experimental data, the uncertainty of the present equations for ammonia, propane, butane, and isobutane in the temperature range from 200 to 600 K and in the pressure range up to 50 MPa is estimated to be ±2 to 3% in the liquid phase, ±3 to 5% in the gaseous phase, and about ±10% in the critical region. The uncertainty of the proposed equation for propylene in the temperature range from 250 to 600 K and in the pressure range up to 50 MPa outside the critical region is estimated to be ±2 to 3% in the liquid phase and ±3 to 5% in the gaseous phase.

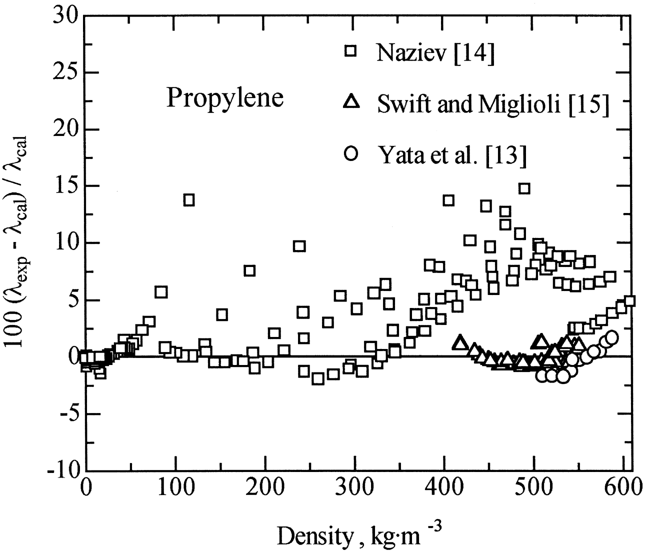

Fig. 10. Deviations of experimental data of the thermal conductivity of propylene from the present model.

5. CONCLUSIONS

The available experimental results for the thermal conductivity of ammonia, propane, butane, isobutane, and propylene are reviewed, with special focus on the liquid phase. New equations for the thermal conductivity of the five substances applicable for practical use over wide ranges of temperature and pressure including the critical region are proposed based on the experimental data.

Compared with existing equations for ammonia, isobutane, and propylene, which are not reliable in the liquid phase, the behavior of the thermal conductivity for these substances is much improved using the present equations.

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