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A Simple Equation for the Thermal Conductivity of Saturated Vapor Refrigerants

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The ability of a material to supply heat by means of conduction is called thermal conductivity, which is defined by Fourier's equation. Thermodynamic data on environmental refrigerants have attracted considerable interest in the design and optimization of refrigeration equipment, such as heat compressors and exchangers. After analysis of statistical effects, a new simple correlation was developed for the thermal conductivity of refrigerants as a function of temperature. An optimization algorithm was used to obtain the constant parameters of the new equation by fitting them to the source databank. The accuracy of the presented equation was compared with commonly used models. Results indicated that the developed model provides more accurate results than those of other considered equations, with an average absolute percentage deviation of 3.46%.

Keywords: Refrigerant, Correlation, Thermal conductivity, Empirical

INTRODUCTION

During the last decades, following the perception of the effect of refrigerants on ozone layer depletion, many researchers began focusing on the measurement of the thermophysical properties of refrigerants to determine a proper replacement. However, equilibrium and transport properties are necessary in the replacement of old refrigerants with new environmentally friendly compounds [1].

Thermal conductivity is an essential parameter for the calculation of heat transfer, especially for refrigerants. High thermal conductivity values result in high heat transfer coefficients [2].

Hence, many empirical correlations for the estimation of the thermal conductivity of refrigerants have been presented in scientific literature. These correlations include: 1) equations based on specific material properties, such as density and/or heat capacity and temperature [3], which are difficult to use for fluids with limited available data; 2) theoretical estimations that consider intermolecular distances [4] or the degrees of association of liquids [5]; and 3) equations based on group contribution theory [6] or molecular descriptors [7,8], which are often unsuitable for all compounds and rather laborious [2].

Rao *et al.* [9] presented generalized correlations by using artificially designed filler shapes to estimate the thermal conductivities of composite material packing. Huber [10] developed preliminary models for the thermal conductivity, viscosity, and surface tension of pure fluids constituting the four alternatives to diesel fuels. Carson [11] described a model for evaluating the reliability of thermal conductivity data using simple thermal conductivity models and heat transfer theory. This method is applied to various food types as examples.

In the present work, we proposed a new simple substance-dependent model based on liquid-vapor equilibrium databank. This model accurately reproduces a thermal conductivity behavior over a wide range in the liquid-vapor region. On the basis of this model, a predictive

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correlation is also established. The thermal conductivity data used in this study were obtained from the National Institute of Standards and Technology Chemistry WebBook [12].

THERMAL CONDUCTIVITY CORRELATIONS

Some techniques for estimating thermal conductivity as a function of temperature, heat capacity, and viscosity are available in literature. In this section, commonly used corresponding states for thermal conductivity estimation are presented.

Eucken and Modified-Eucken Method

Eucken [8] proposed Eq. (1) for pure gases by separating the contributions due to translational and internal degrees of freedom into separate terms:

$$\frac{\lambda M'}{\eta C_v} = 1 + \frac{9/4}{C_v/R} = 1 + \frac{9/4}{(C_p/R)-1} \tag{1}$$

Eucken correlation for pure gases is indicated in Eq. (1).

Equation (2) is often referred to as the modified Eucken correlation (M-Eucken) which was used by Svehla [13] in his compilation for high-temperature gas properties.

$$\frac{\lambda M'}{\eta C_v} = 1.32 + \frac{1.77}{C_v/R} = 1.32 + \frac{1.77}{(C_p/R)-1} \tag{2}$$

The modified Eucken (Eq. (2)) predicts higher values of λ than those of Eucken (Eq. (1)). This difference increases when C_v increases to approximately 12.6 J mol^{-1} K^{-1}.

Stiel-Thodos Method

Stiel and Thodos [14] suggested an empirical model for gases, as follows:

$$\frac{\lambda M'}{\eta C_v} = 1.15 + \frac{2.03}{C_v/R} = 1.15 + \frac{2.03}{(C_p/R)-1} \tag{3}$$

Equations (1), (2) and (3) indicate that the Eucken factor ($\lambda M_W/\eta C_v$) decreases with increasing temperature when the heat capacity increases.

Chung Method

Chung *et al.* [7] presented an approach similar to that of Mason and Monchick [15] to obtain an empirical correlation for thermal conductivity:

$$\frac{\lambda M'}{\eta C_v} = \frac{3.75\Psi}{C_v/R} \tag{4}$$

where λ is the thermal conductivity (W m^{-1} K^{-1}), M' is the molecular weight (kg mol^{-1}), η is the low-pressure gas viscosity (N s m^{-2}), C_v is the heat capacity at constant volume (J mol^{-1} K^{-1}), and R is the gas constant (8.314 J mol^{-1} K^{-1}). Ψ is also calculated as follows:

$$\Psi = 1 + a\{[0.215 + 0.28288a - 1.061\beta + 0.26665Z]/[0.6366 + \beta Z + 1.061\alpha\beta]\} \tag{5}$$

where

$$a = (C_v/R) - 3/2 \tag{6}$$

$$\beta = 0.7862 - 0.7109\omega + 1.3168\omega^2 \tag{7}$$

and

$$Z = 2.0 + 10.5T_r^2 \tag{8}$$

New Predictive Method for Molar Volume

A wide database of thermal conductivity, especially for refrigerants, is available in literature [12], because many organic compounds have been used for many years. Furthermore, a large amount of source data on commonly used refrigerants has been produced after the adoption of the Montreal Protocol on Substances that Deplete the Ozone Layer.

This study aimed to determine a new simple correlation for the thermal conductivity of refrigerants. A four-constant nonlinear equation with high accuracy of vapor-liquid equilibrium data even at low viscosities was developed. After multiple regression analyses, an empirical correlation was suggested as follows:

$$\lambda = \frac{a\,T_r + b\,T_r^{1.5}}{T_r^{1.5}(c + d.T_r^{1.5})} \tag{9}$$

Table 1. Thermal Conductivity Range, Temperature Range, Tuned Coefficients and Average Standard Errors of Coefficients of the Newly Proposed Model

	Subs.	λ_{min}	λ_{max}	T_{min} (K)	T_{max} (K)	a	Dev.% of a	b	Dev.% of b	c	Dev.% of c	d	Dev.% of d
1	R11	0.0582	0.1187	198.15	470.6	-138414	0.21	11241	0.03	2248	0.18	-0.1862	0.02
2	R12	0.0552	0.1228	160.94	384.67	-79451	0.14	7180	0.09	2133	0.12	-0.248	0.01
3	R13	0.0608	0.1349	92	301.65	-11024	0.71	1227	0.01	737	0.61	-0.1324	0.01
4	R14	0.0553	0.1377	98.94	227.08	-20851	0.33	2521	0.01	1969	0.21	-0.5389	0.02
5	R22	0.0703	0.1513	158.41	368.87	-67308	0.10	6239	0.03	2060	0.08	-0.2636	0.00
6	R23	0.0582	0.2686	118.02	298.99	-73952	0.17	7696	0.05	2790	0.13	-0.4685	0.09
7	R32	0.1163	0.2429	136.34	350.9	-28869	0.34	3877	0.03	1975	0.30	-0.2879	0.01
8	R41	0.1248	0.2767	175	317.04	-87771	0.21	12099	0.08	5331	0.17	-0.8812	0.03
9	R113	0.0531	0.0824	236.93	486.79	-193349	0.12	15366	0.00	2785	0.15	-0.2186	0.02
10	R114	0.0442	0.0664	273.15	418.59	-183964	0.44	21603	0.02	7644	0.52	-0.7877	0.01
11	R115	0.0479	0.0942	173.76	353.1	-75919	0.52	6888	0.03	1914	0.41	-0.2539	0.01
12	R116	0.0482	0.0835	175.7	292.63	-98162	0.72	10452	0.09	4535	0.60	-0.7974	0.00
13	R123	0.0389	0.1159	166	456.35	-57975	0.71	4641	0.08	893	0.65	-0.0781	0.01
14	R124	0.0611	0.1248	120	394.97	-28362	0.15	2748	0.09	857	0.10	-0.0999	0.00
15	R125	0.0661	0.1160	172.52	338.9	-72292	0.09	6664	0.02	1819	0.10	-0.2526	0.02
16	R134a	0.0742	0.1452	169.85	373.87	-122389	0.23	10093	0.03	1927	0.21	-0.2301	0.01
17	R141b	0.0786	0.1262	169.68	476.99	-131491	0.45	10706	0.04	1935	0.59	-0.1697	0.03
18	R142b	0.0704	0.1389	142.72	409.81	-161746	0.62	14632	0.01	3820	0.55	-0.4163	0.00
19	R143a	0.0774	0.1372	161.34	345.55	-73897	0.03	6798	0.02	1792	0.07	-0.2501	0.00
20	R152a	0.0940	0.1763	154.56	386.02	-48610	0.19	3913	0.01	757	0.18	-0.0918	0.01
21	R218	0.0475	0.0852	125.45	344.65	-23894	0.32	2297	0.08	802	0.28	-0.1093	0.03
22	R227ea	0.0639	0.0925	146.35	375.57	-91444	0.12	8346	0.01	2054	0.17	-0.2491	0.00
23	R236ea	0.0308	0.1023	242	412.44	-457714	0.91	39008	0.12	5800	1.11	-0.5578	0.04
24	R236fa	0.0682	0.1113	185.35	397.71	-113675	1.03	9863	0.15	2081	1.21	-0.2314	0.04
25	R245ca	0.0852	0.1264	205.36	444.68	-210850	0.60	16557	0.04	2115	0.51	-0.1955	0.02
26	R245fa	0.0614	0.1239	200	426.82	-184515	0.13	15392	0.01	2286	0.080	-0.218	0.00
27	RC318	0.0618	0.0790	233.35	388.12	-264559	0.42	24273	0.03	6053	0.36	-0.7011	0.01

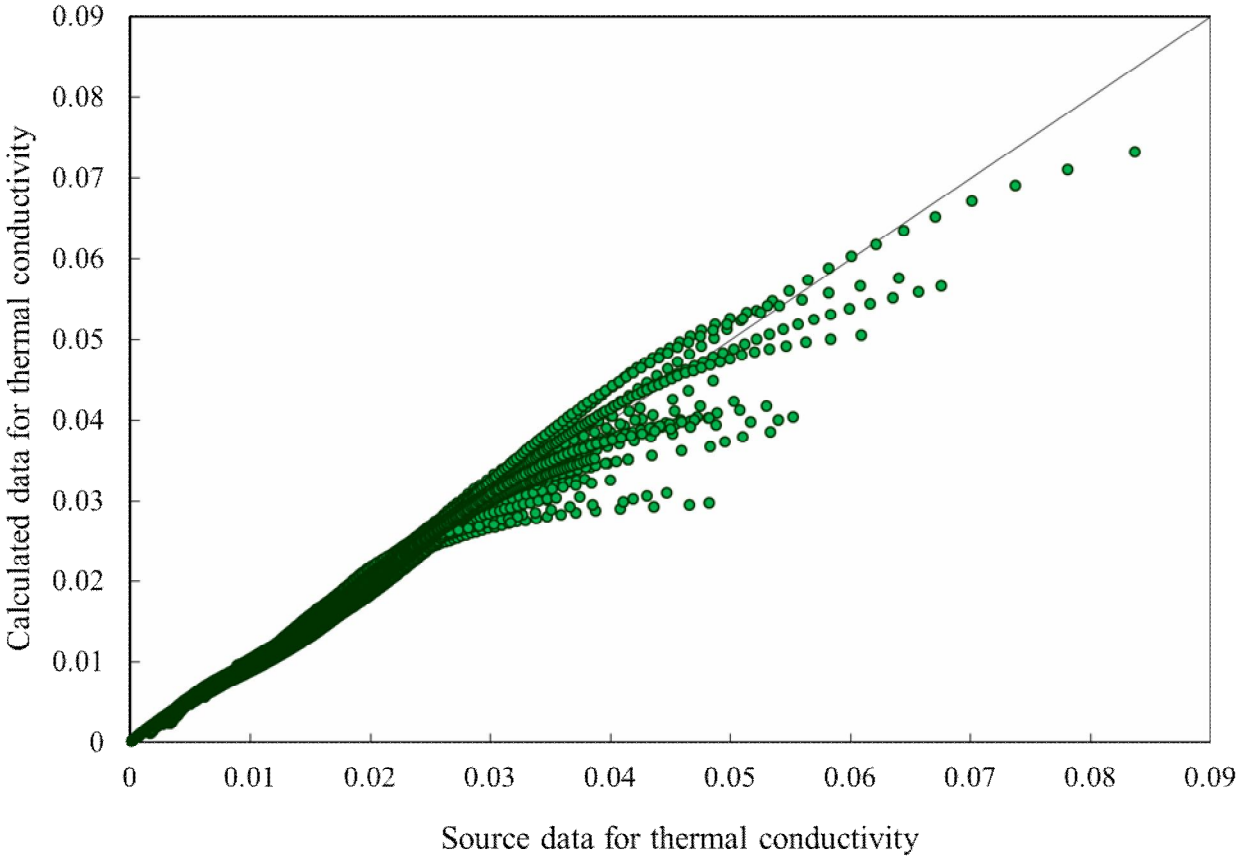

Fig. 1. Accuracy of the presented model *vs*. experimental data.

where coefficients a, b, c and d are constant parameters obtained by using Levenberg-Marquardt algorithm, which minimizes the sum of the squared differences between the observed and predicted values of dependent variables. The constant parameter values of Eq. (9) for 27 pure refrigerants are presented in Table 1. In Eq. (9), T is in Kelvin, and thermal conductivity (λ) is in W m^{-1} K^{-1}.

Table 1 also shows the number of data points, viscosity range, heat capacity range, molecular weight and acentric factor of source data for each substance.

The new empirical model is considerably simpler than those reported in the literature. Other considered models used heat capacity, viscosity, molecular weight, and acentric factor to estimate thermal conductivity, while the present correlation can predict thermal conductivity only by using temperature.

RESULTS AND DISCUSSION

We carried out calculations for 27 pure refrigerants. The thermal conductivity, viscosity, heat capacity, and molecular weight (for calculation of literature models) values were obtained from the databank [12].

To prove the high accuracy of the presented empirical model, the calculated thermal conductivity values of all substances versus the corresponding values in the databank are presented in Fig. 1.

Figure 1 indicates that most of data points are nearly diagonal, and they exhibit low deviation from the corresponding values in the databank.

The average absolute relative deviation (AARD%) values of the thermal conductivity calculated by the newly developed equation and literature models for each of the 27

Table 2. AARD% of Four Literature Equations Compared with the New Method

No.	Substance	Chung	Eucken	M-Eucken	Stiel-Thodos	This study
1	R11	11.9	21.52	4.49	13.51	2.14
2	R12	11.59	19.01	2.85	11.4	2.83
3	R13	8.83	11.28	8.47	5.18	6.20
4	R14	10.46	12.27	7.9	7.14	1.75
5	R22	2.76	6.83	10.77	5.2	2.63
6	R23	7.37	5.34	9.19	4.02	2.41
7	R32	17.69	14.59	21.53	17.32	1.33
8	R41	7.69	6.14	14.13	8.74	3.16
9	R113	4.16	20.83	0.92	11.47	2.05
10	R114	6.41	22.96	3.72	13.92	2.24
11	R115	8.51	21.48	3.57	12.92	1.80
12	R116	6.31	19.28	1.09	10.72	2.47
13	R123	10.17	16.17	16.48	13.04	5.95
14	R124	7.63	18.18	1.48	9.67	7.00
15	R125	2.8	14.59	5.31	6.58	2.97
16	R134a	7.24	14.63	15.47	11.44	2.99
17	R141b	12.05	21.91	10.92	14.96	7.37
18	R142b	3.34	10.38	9.23	2.75	5.29
19	R143a	7.93	16.95	4.58	9.07	2.43
20	R152a	72.54	79.86	91.01	83.52	9.52
21	R218	9.96	7.45	15.41	3.41	5.24
22	R227ea	11.48	24.63	6.19	15.96	3.36
23	R236ea	14.41	28.64	10.47	20.1	1.32
24	R236fa	8	21.49	4.26	12.42	2.43
25	R245ca	11.76	25.45	7.05	16.79	2.61
26	R245fa	15.89	28.29	10.75	20.05	2.07
27	RC318	5.53	23.13	2.95	13.65	1.64

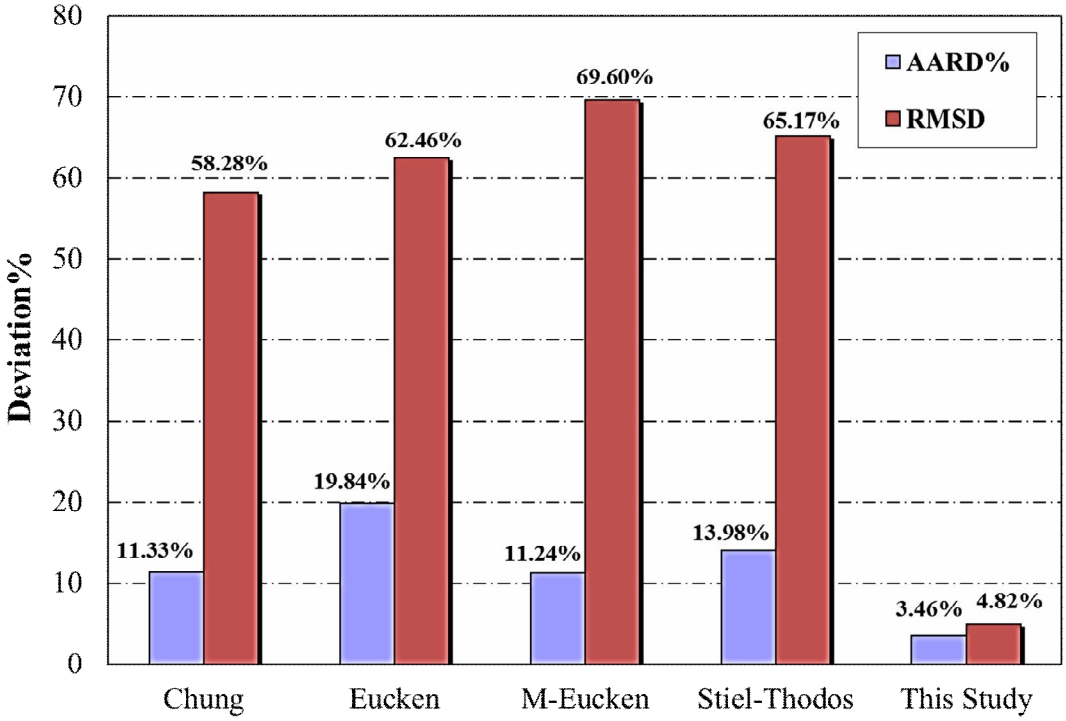

Fig. 2. Statistical parameters of this study compared with those of other methods.

refrigerants against the databank values are presented in Table 2. The newly presented equation is more accurate than those reported in the literature, almost for all types of refrigerants considered in this study.

Figure 2 presents the statistical parameters, including AARD% and root-mean-square deviation (RMSD) of the considered models and newly developed equation.

To further compare the accuracy of four literature methods with the new equation, Fig. 2 presents the statistical parameters, including the AARD% and RMSD of the models for the 27 refrigerants. The criteria for deviations are AARD% and RMSD which are calculated as follows:

$$AARD\% = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{\lambda_{r,i,\exp} - \lambda_{r,i,calc}}{\lambda_{r,i,\exp}}\right| \times 100 \quad (10)$$

$$RMSD = \frac{1}{N}\sqrt{\sum_{i=1}^{N}\left(\frac{\lambda_{r,i,\exp} - \lambda_{r,i,calc}}{\lambda_{r,i,\exp}}\right)^2} \times 100 \quad (11)$$

Figure 3 shows the cumulative frequencies of the proposed and literature models versus AARD. As shown in Fig. 2, the developed equation is more accurate than those of four other commonly used models in the estimation of the thermal conductivity of refrigerants.

The new method successfully predicts 42% and 77% of all experimental data with an AARD% of less than 2 and less than 5, respectively. Only 4.8% of the thermal conductivity data are predicted with an AARD% of more than 10 by the new method. M-Eucken equation, the second most accurate method, predicts 24% and 44% of the data with an AARD% of less than 2 and less than 5, respectively. Finally, the superiority of this new method over the other corresponding states was verified for approximately all data in the databank.

CONCLUSIONS

Several thermal conductivity prediction methods were evaluated. Undesirable prediction deviations were obtained

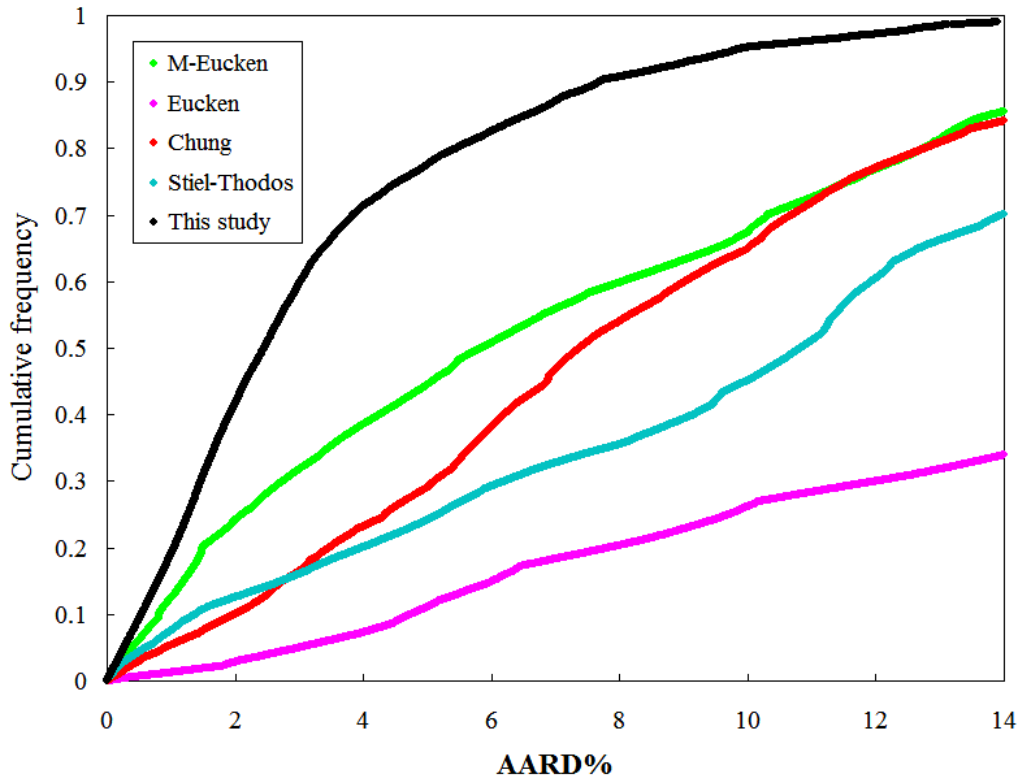

Fig. 3. Cumulative frequencies of various methods in calculating thermal conductivity as a function of AARD%.

using the Eucken equation over a wide range of viscosity and heat capacity. The M-Eucken method generally provides approximately good prediction accuracy relative to the other models. Results indicated that the newly proposed equation is the most suitable model for the 27 pure refrigerants. The proposed correlation presents more number of coefficients than those of the other considered models, however results indicated the superiority of this new equation over all other methods in terms of calculating the thermal conductivity of pure substance with an AARD% of 3.46%.

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