

An Improved Correlation for the Calculation of Liquid Thermal Conductivity

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Eighteen correlations appearing in the literature for the prediction of thermal conductivity, λ , of liquids are critically analyzed, and their reliability is checked using coherent input data and selected experimental λ values. The best results are obtained using the Reid, Sherwood, and Prausnitz correlation with a mean deviation of about 8% between predicted and experimental values. An improved correlation is proposed starting from the Viswanath equation, chosen because of its simplicity and convenience. The values of thermal conductivity obtained by this new correlation agree with the experimental values within 1%.

KEY WORDS: liquids; thermal conductivity; transport properties.

1. INTRODUCTION

The need for accurate and reliable data on physical properties of fluids and solids in the study of thermal processes and in the calculation of heat transfer mechanisms is well known. Heat transfer scientists and engineers are often not in agreement with the results of their studies, because they do not use the same input data for physical properties of the substances, particularly for the thermal conductivity, λ , of fluids. While experimental data are given for a few fluids, for a single fluid they are usually in a limited range of temperature (often only one value at room temperature), and they are obtained with very different and not comparable techniques.

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Some reasons for these problems are proposed:

1. Some authors carry out experimental work on the measurement of thermal conductivity and other physical properties of substances, but their activities do not cover the increasing number of new synthetic organic compounds.
2. A very complete and accurate analysis and classification of experimental data up to 1973 is available, due to Jamieson et al. [1], who scheduled a periodical revision based on further experimental data.
3. A lot of theoretical, semiempirical, and empirical correlations are available in the literature, but their applicability and accuracy was checked by the respective authors using input data of physical properties and experimental data of λ assumed from different and unclassified sources.

The program of our research group was to carry out a homogeneous check of the existing correlations for liquids on the basis of the same input values of physical properties and reliable and classified data of thermal conductivity, and then to suggest a new correlation or a modified one, when not one of the available formulas is acceptable.

2. CHECK OF CRITERIA OF CORRELATIONS

In previous papers [2, 3], a collection of 26 empirical, semiempirical, and theoretical correlations were discussed for the prediction of the thermal conductivity λ of pure liquids at standard conditions, i.e., at a temperature of 20°C and at atmospheric pressure. Merely theoretical correlations based on statistical mechanics have been omitted, because they do not produce reliable results; such formulas are collected by Tye [4] and by McLaughlin [5].

The correlations, rearranged in S.I. units, were tested for a group of twelve liquids belonging to the most important families, and with the same input data for physical properties [6–9], because the differences among the various predicted data on thermal conductivity sometimes may be ascribed to the different evaluations of the parameters entering in the calculations. The comparison between predicted and experimental values of the thermal conductivity was developed by using the experimental data of λ collected and classified by Jamieson et al. [1] in three groups labeled A, B, and C. The group A collects the values with an estimated error within $\pm 2\%$, the group B the values within $\pm 5\%$, and the group C the values less accurate than $\pm 5\%$. Since several data on thermal conductivity exist at each temperature for the same fluid, the average value of the best reliable data available is assumed in this work. This procedure gives more realistic values of deviations between predicted and experimental data than those given by the respective authors,

and results in a very significant comparison between the different correlations.

The analysis of the results at 20°C gives the following indications [2, 3]:

1. The correlations based on a simplified theory are generally less accurate than the merely empirical ones.
2. The correlations that contain explicitly the temperature produce values of the thermal conductivity more exact than the values obtained by the other formulas.
3. The deviations between experimental and estimated λ values are less than 5% only for the Robbins and Kingrea correlation [15]; for the other equations the deviations are generally greater than 10%.

Recently, the authors reported on an investigation made for the best of the cited correlations, taking into account the variation in temperature [10]. The results obtained can be summarized as follows:

1. The degree of reliability of the different formulas is generally not confirmed for the explored range of temperature: the deviations between experimental and estimated λ values increase when the temperature moves away from 20°C.
2. The temperature dependence is not always correct.

In this work, all 26 correlations, together with another two that have since appeared in the literature, are tested according to the above mentioned criteria, taking into account the temperature dependence on the thermal conductivity. The comparison between experimental and predicted λ values is made in a wide range of temperatures (generally between the melting point T_m and the normal boiling point T_b), developing the calculations in steps of 10°C.

3. GENERAL RESULTS OF THE CORRELATIONS

In the following tables, the results of the investigation are shown for the correlations in which the temperature dependence is significant. The investigated formulas are grouped in the following manner: the first group collects the correlations due to Weber and those derived from Weber's formulas, the second group collects the correlations due to Bridgmann and those based on the same hypothesis, and the third group collects the correlations that cannot be derived from a single idea.

The liquids taken in consideration, Jamieson's classification of the experimental data of λ , and the explored range of temperature are summarized in Table I.

In Table II, the correlations (Eqs. 1–18) are given with the relative identification, the mean deviation Δ_{293} at 20°C, the mean deviation Δ_T in the explored range of temperature, and the maximum deviation Δ_{\max} .

Table I. Compounds Investigated with Jamieson's Classification and Ranges of Temperature

Compound	Jamieson's classification	Temperature range	
		Absolute (K)	Reduced
Acetone	A	193–323	0.38–0.64
Benzene	A	283–343	0.50–0.61
Toluene	A	183–383	0.31–0.65
Carbon tetrachloride	A	253–323	0.45–0.60
Chloroform	A	243–323	0.45–0.60
Ethyl alcohol	A	203–333	0.39–0.65
Methyl alcohol	A	203–333	0.40–0.65
n-Pentane	A	163–283	0.35–0.60
n-Hexane	B	183–343	0.36–0.68
n-Octane	A	273–363	0.48–0.64
Refrigerant 11	B	183–283	0.39–0.60
Refrigerant 113	B	243–313	0.50–0.64

Since the thermal conductivity of liquids generally decreases with an increase of temperature, and the twelve compounds taken in consideration follow this temperature dependence, the algebraic signs are added near the formulas: the positive sign + indicates that the temperature dependence is incorrect, the negative sign – indicates that the temperature dependence is correct, while the double sign ± indicates that for some liquids the temperature dependence is incorrect, for others correct.

Equation (1), due to Weber [11] and based on experiments carried out on 50 liquids, can be considered a simplification of the general Debye's expression [12], valid for dielectric solids:

$$\lambda \propto \rho w C_v l \quad (19)$$

where the specific heat at constant pressure C_p replaces the specific heat at constant volume C_v , and it is supposed that the product between the wave propagation velocity w and the wave mean free path l is proportional to the inverse of the mean distance between two adjacent molecules disposed in a cubic lattice $(\rho/M)^{1/3}$.

Equations (2) and (3), due, respectively, to Palmer [13] and to Vargaftik [14], differ from the Weber's equation (1) in the introduction of a corrective factor that takes into account the degree of association (hydrogen bond) of the liquids. In Vargaftik's equation (3), α may be assumed as $\alpha = M \cdot \Delta H_{vb} / (87922.8 T_b)$ (similar to Palmer's equation) at 30°C for most liquids or at $T_c/2$ for low boiling fluids. Calculated values of $\alpha < 1$ should be taken as unity, and at temperatures other than 30°C (or $T_c/2$) α may be assumed to

Table II. General Table of Correlations^a

Equation No.	Identification	Correlation	Temp. dep.	$\Delta_{293}(\%)$	$\Delta_T(\%)$	$\Delta_{\max}(\%)$
First group						
(1)	Weber [11]	$\lambda = 3.5808 \times 10^{-8} C_p \rho \left[\frac{\rho}{M} \right]^{1/3}$	\pm	13.1	16.8	50.9
(2)	Palmer [13]	$\lambda = 3.9642 \times 10^{-3} C_p \rho \left[\frac{\rho}{M} \right]^{1/3} \frac{T_b}{M \Delta H_{vb}}$	\pm	22.2	28.3	93.9
(3)	Vargaftik [14]	$\lambda = 4.2713 \times 10^{-8} C_p \rho \left[\frac{\rho}{M} \right]^{1/3} \frac{1}{\alpha}$	\pm	15.1	22.6	79.2
(4)	Robbins and Kingrea [15]	$\lambda = \frac{4.1868 \times 10^{-5} (88.0 - 4.94H) \left[\frac{0.551^N}{T_r} \right] \cdot C_p \cdot \rho \left[\frac{\rho}{M} \right]^{1/3}}{M(\Delta H_{vb}/T_b) + R \cdot \ln(273/T_b)}$	$-$	4.6	9.0	50.5
Second group						
(5)	Bridgmann [17-19]	$\lambda = 3 K \frac{W}{l^2}$	$-$	31.5	122.0	355.6
(6)	Osida [20]	$\lambda = 1.2979 \times 10^{-2} \cdot \frac{T_m^{1/2}}{M^{1/2} V^{2/3}}$	$-$	27.7	29.0	54.2
(7)	Hirschfelder et al. [21]	$\lambda = 2.8 \cdot K \cdot \frac{W}{v^{2/3}} \cdot \gamma^{1/2}$	$-$	21.9	22.1	106.2
(8)	Viswanath [33]	$\lambda = 3.6 \times 10^{-7} \frac{M^{1/2} \Delta H_{vb}}{C \cdot V^{2/3} T^{1/2}} \left[\frac{1 - T_r}{1 - T_{br}} \right]^{10.38}$	$-$	39.3	39.0	249.5
(9)	Badea [22]	$\lambda = 1.0798 \times 10^{-7} C_p^{3/2} \rho^{2/3} T^{1/2} M^{1/3}$	$+$	14.9	19.4	65.4
(10)	Narasimhan et al. [24]	$\lambda = 2.8379 \times 10^{-7} \cdot C_{p293}^{0.83} \cdot \rho_{293} \left[\frac{293}{T} \right]$	$-$	12.1	12.2	65.1

Table II. Continued

Equation No.	Identification	Correlation	Temp. dep.	$\Delta_{293}(\%)$	$\Delta_T(\%)$	$\Delta_{\max}(\%)$
Third group						
(11)	Scheffy and Johnson [25, 26]	$\lambda = 1.951 \cdot \frac{1 - 0.00126(T - T_m)}{T_m^{0.216} M^{0.3}}$	—	14.7	14.8	59.7
(12)	Badea [22]	$\lambda = 3.3062 \times 10^{-10} \cdot M^{1/3} \cdot \rho^{2/3} \cdot C_p \cdot \Delta H_v$	±	17.4	17.1	71.2
(13)	Pachaiyappan [27]	$\lambda = 3.009 \times 10^{-10} \cdot C_p \cdot \rho \cdot \Delta H_{vb}^{1/2} \cdot V_b^{1/3}$	±	12.2	15.0	52.3
(14)	Pachaiyappan [27]	$\lambda = 2.2796 \times 10^{-10} \cdot C_{p293} \cdot \rho_{293} \cdot \Delta H_{v0}^{1/2} \cdot V_b^{1/3} \left[\frac{T_c}{T} \right]^{1/2}$	—	11.7	12.9	29.9
(15)	Pachaiyappan and Vaidyanathan [29]	$\lambda = 8.84 \times 10^{-8} \cdot C_p \cdot \rho$	±	14.3	11.7	85.0
(16)	Vaidyanathan and Velayutham [28]	$\lambda = 7.5 \times 10^{-8} \cdot C_{p293} \cdot \rho_{293} \left[\frac{T_b}{T} \right]^{1/2}$	—	11.7	11.7	58.1
(17)	Reid et al. [30]	$\lambda = \frac{1.1053}{M^{1/2}} \cdot \frac{3 + 20(1 - T_c)^{2/3}}{3 + 20(1 - T_w)^{2/3}}$	—	7.8	8.1	29.9
(18)	Reid et al. [30]	$\lambda = \lambda_{wT} \cdot \frac{3 + 20(1 - T_c)^{2/3}}{3 + 20(1 - 293/T_c)^{2/3}}$	—	17.0	11.3	39.2

*In S.I. units.

vary linearly between the value $M \cdot \Delta H_{vb}/(87922.8 T_b)$ at 30°C (or $T_c/2$) and the value 1.0 at T_c . In the cited expressions, ρ is the density, M the molecular weight, ΔH_{vb} the latent heat of vaporization at the normal boiling point, T_c the critical temperature, T_r the reduced temperature, and R the gas constant.

In eq. (4), due to Robbins and Kingrea [15], three corrective factors are introduced with respect to the Weber's correlation: (a) the factor $M \cdot \Delta H_{vb}/T_b + R \ln(273/T_b)$, in order to take into account the degree of association of the liquids; (b) the factor $(0.55/T_r)^N$, where N is equal to 1 or to 0 if the density at 20°C is less than 1,000 or greater than 1,000, respectively, in order to adequately represent the temperature dependence of the thermal conductivity; and (c) the factor $(88.0 - 4.94 H)$, the numerical value of which, for a particular family, depends upon the contribution of certain radicals present as substitution in (or added to) a basic straight-chain or ring structure; the values of H are tabulated by Robbins and Kingrea [15]. The range of applicability for eq. (4), stated by the authors, is $0.4 < T_r < 0.9$. In the cited correlations, C_p and ρ are temperature dependent, and their values are obtained by the formulas presented by Touloukian and Makita [8] and Perry and Chilton [7], respectively. The mean and maximum errors in C_p are 0.4% and 2.7%; the mean and the maximum errors in ρ are 1.0% and 6.0%.

The equations of the second group derive from simple theoretical considerations accompanied by strong approximations. The main problem lies in the calculation of the sound velocity as a temperature function; the use of the Rao's formula [16] produces an error difficult to evaluate, but certainly greater than 3%. Another source of uncertainty present in eq. (5), due to Bridgmann [17-19], lies in the mean distance of the centers of contiguous molecules l , estimated by the formula $l = \sqrt[3]{M/(N\rho)}$, where N is Avogadro's number, according to the approximation of the cubic lattice. In Eq. (6), due to Osida [20], the molal volume V_m is given by $V_m = M/\rho$, and in Eq. (7), the molecular volume v by $v = M/(N\rho)$.

The authors [21] of the correlation (7) require that the ratio of specific heats γ must assume the values derived from measurements of the sound velocity. Since it is very difficult to find the required values of γ in the literature, in this work γ is assumed to be a constant equal to $4/3$. In Eq. (8), C is a particular "packing factor," depending on the molecular structure. The correlation (9), due to Badea [22], is established by utilizing the Kardos [23] hypothesis and the approximations of the kinetic theory of gases. Equation (10), due to Narasimhan et al. [24], derives from theoretical considerations and empirical calculations; in this equation, C_p and ρ are evaluated at 20°C, and the corrective factor $(293/T)^{0.38}$ is introduced to predict the thermal conductivity at other temperatures.

The third group begins with the correlation (11), due to Scheffy [25] and Scheffy and Johnson [26], which is essentially empirical, though based originally upon a theoretical equation relating the thermal conductivity at the melting point to fundamental molecular properties, such as vibrational frequency and intermolecular distances. Equation (11) is not suitable for highly polar or inorganic molecules such as water, or for reduced temperatures greater than 0.7. The correlation (12), due to Badea [22], is obtained by dimensional analysis applied upon the function $\lambda = f(\rho, m, C_p, \Delta H_{vb})$. Equation (13), due to Pachaiyappan [27], is derived from the function $M = f(\lambda, V_m, C_p, \Delta H_v, \sigma)$, where V_m is the molal volume, and σ is the Lennard-Jones parameter. In the formula (14), due to Pachaiyappan [27], C_p and ρ are estimated at 20°C, and the temperature dependence is pointed out by means of the factor $(T_c/T)^{0.5}$. The same procedure is applied by Vaidyanathan and Velayutham [28] in Eq. (16) with respect to the Eq. (15), obtained by Pachaiyappan and Vaidyanathan [29] on the basis of the correlation (13). Equations (17) and (18), due to Reid et al. [30], are based first, on the suggestions of Sato (as discussed in Reid et al. [30]) and Riedel [31], and second, on the suggestions of Missenard [32] and Riedel [31]. In Eq. (18), λ_{Mf} is the thermal conductivity at 20°C predicted by Missenard's correlation [32], valid at room temperature:

$$\lambda = 2.846 \times 10^{-7} (T_b \rho)^{0.5} C_p / (N_a)^{0.25} \quad (20)$$

where N_a is the number of atoms in the molecule.

4. DISCUSSION OF THE PRECEDING PREDICTION METHODS

On the basis of the comparison between the selected experimental values of λ and those calculated by the cited correlations, seven equations (due to Scheffy and Johnson [26], Reid et al. [30], Narasimhan et al. [24], Pachaiyappan [27], Vaidyanathan and Velayutham [28], and Viswanath [33]) are selected and proposed for engineering purposes. The above mentioned formulas have been selected according to the following considerations:

1. They contain parameters easy to find, with satisfactory accuracy, even as functions of the temperature.
2. The thermal conductivity predicted through them decreases with the increase of the temperature, according to the experimental evidence.
3. The deviation $\Delta\%$ is acceptable or, in the case of the Viswanath's correlation, a satisfactory improvement is possible.

The correlations (5) and (7), due to Bridgmann and to Hirschfelder et al., respectively, are not suitable because of the difficulty in finding the sound

Table III. General Results of the Check for Some Interesting Correlations that Have Appeared in the Literature

Compound	Temp. range Absolute (K)		Eq. (8)	Eq. (10)	Eq. (11)	Eq. (14)	Eq. (16)	Eq. (17)	Eq. (18)						
	Reduced		Δ (%) Δ_{max} (%)	Δ (%) Δ_{max} (%)	Δ (%) Δ_{max} (%)	Δ (%) Δ_{max} (%)	Δ (%) Δ_{max} (%)	Δ (%) Δ_{max} (%)	Δ (%) Δ_{max} (%)						
Acetone	193	323	52.8	5.2	8.7	4.5	9.2	3.4	5.5	15.6	17.1	2.0	3.6	2.9	4.3
	0.38	0.64													
Benzene	283	343	30.1	34.3	4.8	7.0	7.5	10.6	4.1	5.7	13.1	14.6	1.4	2.2	5.4
	0.50	0.61													
Toluene	183	383	32.7	53.7	3.9	14.2	5.2	16.0	7.9	17.9	4.3	5.9	4.0	10.0	4.8
	0.31	0.65													
Carb. tetr.	253	323	5.7	11.0	6.2	8.4	18.8	20.5	15.0	16.2	7.5	8.0	2.9	4.5	8.7
	0.45	0.60													
Chloroform	243	323	29.7	36.1	1.9	3.9	11.8	15.3	18.6	19.3	3.0	3.9	4.2	4.8	2.1
	0.45	0.60													
Eth. alcohol	203	333	5.9	16.7	3.3	10.5	2.6	8.5	24.8	29.9	5.9	7.9	15.5	17.3	17.4
	0.39	0.65													
Meth. alcohol	203	333	206.9	249.5	10.6	11.3	4.8	5.2	9.5	13.8	20.1	22.1	10.6	15.0	10.1
	0.40	0.65													
n-Pentane	163	283	37.9	48.8	16.7	29.1	24.9	40.7	8.0	15.7	3.2	4.5	22.6	29.9	19.8
	0.35	0.60													
n-Hexane	183	343	10.8	21.9	11.0	19.3	12.7	20.0	8.0	12.5	3.2	5.3	9.3	11.9	7.9
	0.36	0.68													
n-Octane	273	363	4.9	8.1	16.4	22.0	6.9	11.2	24.1	28.9	8.4	12.7	4.7	5.4	8.2
	0.48	0.64													
Refrig. 11	183	283	29.3	40.8	10.6	14.3	26.9	32.0	22.8	24.0	4.8	5.9	4.0	5.3	13.5
	0.39	0.60													
Refrig. 113	243	313	20.2	25.0	55.7	65.1	50.8	59.7	8.2	13.1	51.2	58.1	14.9	16.1	37.8
	0.50	0.64													
Mean general results			38.9		12.2		14.8		12.9		11.7		8.1		11.3

velocity data as a function of the temperature. The Badea, Vargaftik, Pachaiyappan et al., Weber, and Palmer correlations, Eqs. (1)–(3), (9), (12), (13), and (15), should be excluded because of the anomalous dependence of calculated values of λ on the temperature with reference to the experimental data. Equation (6), due to Osida, when tested with selected experimental data, gives very large errors. Correlation (4), due to Robbins and Kingrea, is also omitted because, although it is very satisfactory at standard conditions, i.e., close to 20°C, it diverges at other temperatures and contains parameters difficult to find.

In Table III, the complete deviation data are summarized for the selected correlations. Table III shows that the best results of the λ – T dependence are given by Eqs. (17) and (18): the mean deviations and the maximum ones are generally smaller than in the other correlations. Equations (10) and (11) otherwise appear to be very suitable correlations for a rapid estimation of the thermal conductivity, because they contain only the parameters C_p and ρ at 20°C [24] and only T_m and M [26]. Nevertheless, the evidenced errors, even for the best correlations, are very large, and it is desirable to find a more exact equation or to improve one of those already existing. This is the reason why in Table III there is Viswanath's equation (8) too, though the deviations are the worst ones.

5. THE VISWANATH CORRELATION

Viswanath [33] reconsiders Eq. (7) in the form

$$\lambda = 2.8 (N/V_m)^{2/3} K w \gamma^{1/2} \quad (21)$$

changing the equation constant 2.8 to the value 2.4; K is Boltzmann's constant. Next, according to the suggestions of Glasstone et al. [34] (the theory of molecular holes in the liquids), Viswanath rearranges the correlation (21), using the following expression for w :

$$w = \left(\frac{\gamma}{M C^2 R} \right)^{1/2} \frac{\Delta H_{vb}}{T^{1/2}} \quad (22)$$

where C is a particular "packing factor," depending on the liquid molecular structure. Equation (21) becomes

$$\lambda = 3.6 \times 10^{-7} \frac{M^{1/2} \Delta H_v}{C V_m^{2/3} T^{1/2}} \quad (23)$$

where ΔH_v is expressed by the empirical relation of Watson [35],

$$\Delta H_v = \Delta H_{vb} \left(\frac{1 - T_r}{1 - T_{br}} \right)^{0.38} \quad (24)$$

where T_{br} is the normal reduced boiling point, so that the Eq. (23) becomes

$$\lambda = 3.6 \times 10^{-7} \frac{M^{1/2} \Delta H_{vb}}{C V_m^{2/3} T^{1/2}} \left(\frac{1 - T_r}{1 - T_{rb}} \right)^{0.38} \quad (25)$$

Moreover, Viswanath utilizes the values of V_m at the normal boiling point. The value of the characteristic packing factor C , calculated by Viswanath for some fluids, starting from experimental data of λ , is normally assumed to be 2, according to the author's indications.

The results of the calculations through Eq. (25) are presented in Table III. The mean deviation and the maximum deviation appear to be very large, except for carbon tetrachloride, ethyl alcohol, and n-octane, for which the values of C , calculated by Viswanath through experimental data, are used. Although the results are not positive, the following advantages are to be evidenced:

1. Equation (25) is very simple and contains parameters easy to find with satisfactory accuracy.
2. The dependence of the calculated thermal conductivity on temperature is generally of the same kind as that for the experimental ones.

These considerations suggest the opportunity to try an improvement. The improvement of the Viswanath's correlation is developed in two ways:

1. Recalculation of the packing factor C through the selected experimental data of λ for the single fluids to reduce the deviations
2. Recalculation of the temperature exponent in order to eliminate the possible temperature dependence of C and to make the calculated diagram closer to the experimental one

6. THE PACKING FACTOR CALCULATION

The packing factor has been recalculated using the selected thermal conductivity experimental values of the considered fluids in the same ranges of temperature indicated in Table III. The factor C appears to be dependent on the temperature, so that its mean value C_m is assumed in Eq. (25) for the new estimation of λ :

$$\lambda = 3.6 \times 10^{-7} \frac{M^{1/2} \Delta H_{vb}}{C_m V_m^{2/3} T^{1/2}} \left(\frac{1 - T_r}{1 - T_{br}} \right)^{0.38} \quad (25')$$

Table IV. Factor C_m in Eq. (25') and Values of Deviations for λ

Compound	C_m	Δ (%)	Δ_{\max} (%)
Acetone	3.06	3.1	8.4
Benzene	2.59	1.7	3.7
Toluene	2.65	5.4	16.0
Carb. tetrachl.	2.45	2.8	5.6
Chloroform	2.59	2.7	5.1
Eth. alcohol	5.45	5.3	11.4
Meth. alcohol	6.14	6.8	13.8
n-Pentane	2.73	2.7	6.3
n-Hexane	2.24	5.0	10.1
n-Octane	1.90	2.5	4.4
Refrig. 11	2.59	4.7	8.7
Refrig. 113	2.41	1.9	3.7
Mean general deviation		3.8	

The results for C_m and for the mean deviations $\Delta\%$ and the maximum deviations $\Delta_{\max}\%$ are summarized in Table IV. The values of the deviations are much better than those obtained by the values of C suggested by Viswanath: the mean general deviation between experimental and calculated data is 3.8% and the maximum deviations do not exceed the value 16.0%.

The above results indicate that a correlation can be attempted that relates the packing factor C to the absolute temperature T in order to point out completely the temperature dependence in Eq. (25). Several attempts, made on the basis of the diagram C versus T for the considered liquids, lead to an equation of the following type:

$$C = a \cdot T^b \quad (26)$$

Table V. Factors a and b in Eq. (26) with the Correlation Coefficient r^2

Compound	a	b	r^2
Acetone	14.71	-0.28	0.99
Benzene	15.76	-0.31	0.96
Toluene	12.67	-0.28	0.93
Carb. tetrachl.	19.11	-0.36	0.95
Chloroform	17.82	-0.34	0.99
Eth. alcohol	46.23	-0.38	0.98
Meth. alcohol	111.89	-0.52	0.99
n-Pentane	7.21	-0.18	0.96
n-Hexane	12.09	-0.30	0.96
n-Octane	8.46	-0.26	1.00
Refrig. 11	22.49	-0.40	0.98
Refrig. 113	9.95	-0.25	0.98

Equation (26) is obtained by the least squares method in the ranges of temperature indicated in Table III, and the parameters a and b are presented in Table V with the values of the correlation coefficient r^2 . The parameters a and b (practically temperature independent) are characteristic of each fluid, and the next problem lies in finding a relationship among a , b , and some physical properties of the liquids.

The solution of this problem is difficult and, because of the proximity of its values, the exponent b is assumed equal to the mean value $-1/3$. The values of a are recalculated by the least squares method, so that

$$C' = a'T^{-1/3} \quad (27)$$

is the resulting equation for the new packing factor C' . The a' values are presented in Table VI, and the mean error for C' with respect to the data of C calculated by the selected experimental values of λ is now equal to about 3.5%.

Finally, Eq. (25) and (27) give the following correlation:

$$\lambda = \frac{3.6 \times 10^{-7} M^{1/2} \Delta H_{vb}}{a' V_b^{2/3} T^{1/6}} \left(\frac{1 - T_r}{1 - T_{br}} \right)^{0.38} \quad (28)$$

A preliminary test of the preceding formula gives a mean deviation between calculated and experimental data of λ equal to 2%, so that at this point it appears useful to propose Eq. (28) in the form

$$\lambda = B \frac{M^{1/2} \Delta H_{vb}}{V_b^{2/3} T^{1/6}} \left(\frac{1 - T_r}{1 - T_{br}} \right)^{0.38} \quad (29)$$

Table VI. Factor a' in Eq. (28)

Compound	a'
Acetone	19.34
Benzene	17.58
Toluene	17.22
Carb. tetrachl.	16.27
Chloroform	17.01
Eth. alcohol	34.97
Meth. alcohol	39.43
n-Pentane	16.30
n-Hexane	14.21
n-Octane	12.96
Refrig. 11	15.86
Refrig. 113	15.70

where B is calculated utilizing the experimental selected values of the thermal conductivity. The factor B is characteristic of each fluid and its dependence on the temperature is practically negligible (within a few thousandths in the entire considered range).

The investigation of Eq. (25) indicates an alternative method that equally leads to the correlation (29) by means of simple mathematical considerations based on the study of the diagrams of λ versus T_r . When these diagrams are traced utilizing the selected experimental data of λ and the values of the thermal conductivity are calculated by the Eq. (25'), two curves for each fluid are obtained of the type represented in Fig. 1. The intersection of the two curves is in correspondence with $T_r = 0.5$.

On the basis of the above generalized results, the second term of the Eq. (25') is multiplied by the corrective factor $(T_r/T_{ro})^\alpha$, where $T_{ro} = 0.5$ for all the fluids and the exponent α should be chosen in such a way as to improve the values of the deviations between experimental and predicted data of the thermal conductivity.

This purpose is attained by putting $\alpha = 1/3$, so that we have

$$\lambda = \frac{3.6 \times 10^{-7}}{C_m} \frac{M^{1/2} \Delta H_{vb}}{V_b^{2/3} T^{1/2}} \left(\frac{1 - T_r}{1 - T_{br}} \right)^{0.38} \left(\frac{T_r}{0.5} \right)^{1/3} \quad (29')$$

or

$$\lambda = \frac{3.6 \times 10^{-7}}{C_m 0.5^{1/3} T_c^{1/3}} \frac{M^{1/2} \Delta H_{vb}}{V_b^{2/3} T^{1/6}} \left(\frac{1 - T_r}{1 - T_{br}} \right)^{0.38} \quad (29'')$$

Equation (29'') is fully analogous to Eq. (29).

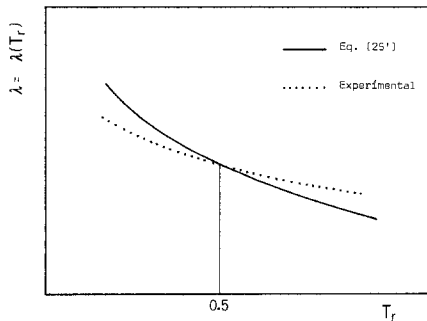


Fig. 1. λ versus T_r according to Eq. (25') (solid line) compared with experimental data (dotted line).

7. CORRELATION PROPOSED AND RESULTS OBTAINED

At this point, Eq. (29) is rearranged in terms of the reduced temperature T_r , which is more convenient in the case of generalized equations. The correlation proposed in the temperature range $0.3 \leq T_r \leq 0.7$ is the following:

$$\lambda = A_r \cdot \frac{M^{1/2} \Delta H_{vb}}{V_b^{2/3} T_r^{1/6}} \left(\frac{1 - T_r}{1 - T_{br}} \right)^{0.38} \quad (30)$$

The factor A_r is characteristic of each fluid, and its value is obtained by the experimental data of the thermal conductivity.

In order to carry out a significant check of Eq. (30), 20 fluids are chosen to include the members of the most important organic families. A_r is calculated for all the liquids considered by means of the selected experimental data of the thermal conductivity, and its value is practically temperature independent. Table VII presents the values of A_r with the mean and the maximum deviations.

Table VII. Factor A_r and Mean and Maximum Deviations Between Experimental and Calculated Values of λ According to Eq. (30)

Compound	Jamieson's class	$A_r \times 10^9$	Temp. range (reduced temp.)	Δ (%)	Δ_{\max} (%)
Acetone	A	6.584	0.38–0.64	0.7	1.7
Benzene	A	7.125	0.50–0.61	0.3	0.9
Toluene	A	7.195	0.31–0.65	1.5	5.9
Ethyl benzene	A	7.664	0.31–0.57	0.3	0.7
Carb. Tetrachl.	A	7.716	0.45–0.60	0.5	1.4
Chloroform	A	7.423	0.45–0.60	0.2	1.2
Ethyl alcohol	A	3.637	0.39–0.65	1.0	2.1
Methyl alcohol	A	3.239	0.40–0.65	2.4	5.0
n-Propyl alcohol	A	4.267	0.47–0.67	1.9	4.3
n-Butyl alcohol	A	4.977	0.38–0.66	3.1	6.2
n-Butane	A	8.274	0.36–0.60	1.8	3.8
n-Pentane	A	7.877	0.35–0.60	2.4	5.7
n-Hexane	B	8.964	0.36–0.68	1.1	2.2
n-Heptane	A	10.348	0.36–0.71	0.1	0.5
n-Octane	A	9.620	0.48–0.64	0.8	1.5
Diethyl ether	A	8.517	0.41–0.65	1.4	4.1
Diphenyl ether	A	8.445	0.43–0.67	1.2	2.6
Ethyl acetate	A	7.665	0.52–0.64	0.4	0.8
Refrig. 11	B	8.150	0.39–0.60	0.9	1.5
Refrig. 113	B	8.149	0.50–0.64	0.7	1.6
Mean general deviation				1.1	

8. CONCLUSIONS

The proposed correlation (30) presents the following advantages with respect to the original one due to Viswanath:

1. The packing factor C , temperature dependent, is substituted by the factor A_r , which is practically temperature independent in a large range of T_r .
2. The temperature dependence is completely described because of the new exponent of T_r .
3. The improvement is considerable: the mean general deviation $\Delta_T = 1.1\%$ and the maximum deviation $\Delta_{\text{Max}} = 6.2\%$ between predicted and selected experimental λ values are substantially smaller than the deviations evidenced by the prediction methods appearing in the literature.
4. The correlation (30) is checked by means of 20 liquids, but they are representative of the most important organic families and recently good results were obtained taking into consideration 30 refrigerant fluids.
5. The explored range of temperature $0.3 \leq T_r \leq 0.7$ can be enlarged: preliminary results for some refrigerant families indicate that in the reduced temperature range $0.3 \leq T_r \leq 0.9$, the mean general deviation is $\Delta_T = 1.2\%$.
6. The calculation of the factor A_r for a single fluid can be developed by using only a few accurate experimental values of the thermal conductivity close to $T_r = 0.5$ (if necessary, only one value of λ at $T_r = 0.5$); in this manner, it is possible to predict the λ values at different temperatures with deviations smaller than 2%.

It will be interesting to give a general correlation between the factor A_r and the physical properties of the fluids, e.g., the properties already used in Eq. (30), with a suitable new exponent, or other properties that can be easily found in the literature.

This is a very difficult problem to solve, but it appears reasonable at this point to look for a less general equation based on the following hypothesis: a correlation exists between A_r and the physical properties of the fluids, but this correlation is characteristic of each liquid's family. Preliminary calculations, developed for some organic families of fluids (alcohols, refrigerants, and ketones), are giving satisfactory results.

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