CORRELATION OF THE THERMAL CONDUCTIVITY OF SATURATED VAPOURS

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ABSTRACT

Using the dimensionless coordinates $\lambda *$ and $T *$, having the following definitions

$$\lambda^* = \left(\frac{\lambda_{ec}}{\lambda} - 1\right) \Big/ \left(\frac{\lambda_{ec}}{\lambda_{NB}} - 1\right)$$

where λ_{ec} is the equivalent thermal conductivity at the critical point $T_c(K)$, λ_{NB} is the thermal conductivity at the normal boiling temperature T_{NB} (K) and λ is the thermal conductivity at any given temperature T (K) and

$$T^* = \left(\frac{T_c}{T} - 1\right) \Big/ \left(\frac{T_c}{T_{NB}} - 1\right)$$

where T_c is the critical point temperature in K, an empirical equation

$$\lambda^* = \frac{mT^*(b + T^*)}{k + T^*}$$

has been established to calculate the thermal conductivity of saturated vapours over the entire saturated vapour–liquid equilibrium range, from the triple point to the close vicinity of the critical point, for separate compounds including inert and halogen compound families. The proposed relation compares excellently in overall accuracy with other selected correlations over the entire range of investigation.

INTRODUCTION AND PROPOSED CORRELATION

Current advances in chemical engineering design to critical and supercritical states require a better understanding of heat transfer operations. Thermal conductivity is an important factor needed in the solutions of these heat transfer equipment design problems. Yet it is a difficult property to be measured, especially at high temperatures and at the saturated vapour–liquid critical point. The overall paucity of the high temperature and pressure experimental data [1] is further accentuated by their questionable accuracy.

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Consequently, a set of theoretical and semi-empirical thermal conductivity prediction methods has been proposed for gases. The rigorous Chapman–Enskog theory [2,3] satisfactorily predicts the thermal conductivity of dilute and moderately dense gases at low and moderate temperatures but it fails at high temperatures [4] largely because of the incomplete understanding of exactly how the internal degrees of freedom may contribute to the various modes of energy transfer in polyatomic molecules [3,4].

Despite the relatively early investigations of the variations in thermal conductivity with temperature of the saturated vapour and liquid states (see for example the work of Liley [5,6]), there are, as yet, no entirely satisfactory semi-empirical methods for calculating the thermal conductivity of pure substances along the vapour–liquid saturated equilibrium curve.

Because these saturated equilibrium curves represent states of coexistence of pairs of phases (i.e. liquid–vapour) and as the system is thermodynamically univariant, we can say that for a pure substance at a given temperature T and for a given value of $\lambda(T)$, a single value of P exists, satisfying the thermodynamic restriction

$$\lambda_s = g(T_s) = h(P_s) \tag{1}$$

where s is the saturation state, and g and h represent g- and h-functions, respectively. Equation (1) specifies that only the saturation temperature or else the pressure is necessary in order to describe uniquely the thermal conductivity, because choosing T_s will at the same time determine the value of P_s for the given substance. On the basis of eqn. (1), it appears entirely feasible that a direct empirical relation between the saturated vapour thermal conductivity and the temperature along the liquid–vapour saturated equilibrium curve for the pure substances, could be developed.

To establish such a relation, we introduce new reduced state coordinates (compare with Lielmezs et al. [7–11]), associated with the phenomenological scaling and renormalization group theory [12], as follows

$$\lambda^* = \left(\frac{\lambda_{ec}}{\lambda} - 1 \right) \bigg/ \left(\frac{\lambda_{ec}}{\lambda_{NB}} - 1 \right) \tag{2}$$

and

$$T^* = \left(\frac{T_c}{T} - 1 \right) \bigg/ \left(\frac{T_c}{T_{NB}} - 1 \right) \tag{3}$$

where λ_{ec} is the equivalent state thermal conductivity at the critical point [†],

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[†] Determined by means of the limiting critical state thermal conductivity obtained either from direct experimental data extrapolations to the critical state (Table 1) or calculated by means of a suitable correlative equation such as that given in the earlier papers by Comings and Nathan [13], Owens and Thodos [14–16], Schaefer and Thodos [17] and Gamson [18], or in the later work by Riazi and Fahri [19].
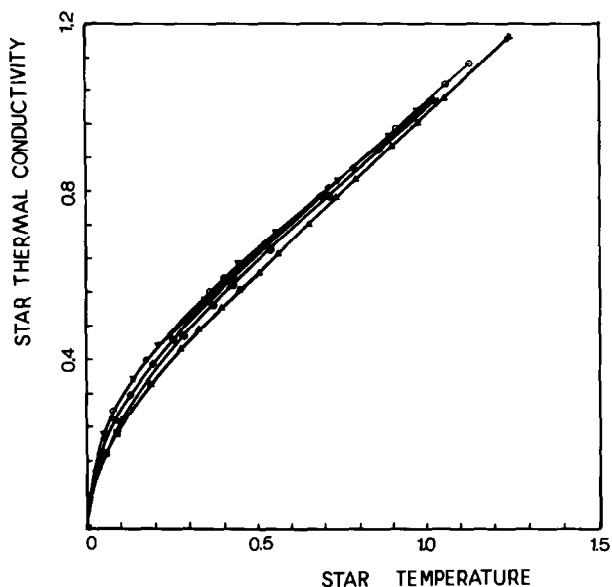
Fig. 1. Reduced temperature T^* vs. reduced thermal conductivity λ^* for rare gases. ◆———◆, neon; ▲———▲, argon; ●———●, krypton; ▼———▼, xenon; ○———○, radon.

λ_{NB} is the thermal conductivity at the normal boiling point temperature, λ is the thermal conductivity at any given temperature and T_c is the critical point temperature.

For the co-ordinate system given in eqns. (2) and (3), the thermal conductivity of saturated vapour of a pure substance, can, therefore, be expressed as follows (see Table 2 and Fig. 1)

$$\lambda^* = \frac{mT^*(b + T^*)}{k + T^*} \tag{4}$$

where constants characteristic of the pure substance in its saturated vapour state, m, b and k, have been obtained from the data sets given in Table 1 by means of non-linear least-square regression methods.

The proposed relation (eqn. (4)) was generalized in terms of physical property for given families of compounds, expressing coefficients k and b of eqn. (4) as non-linear functions of the molecular weight

$$X = P(1)[MW - P(2)]^2 + P(3) \tag{5}$$

where X is the running variable for m, k and b parameters while the coefficients $P(1)$, $P(2)$ and $P(3)$ are determined by means of non-linear regression techniques. Parameters m, k and b are shown in Table 2 for two compound families, the halogens and the inert gases. The k and b parameters are both family and molecular weight dependent while m remains

TABLE 1

Summary of experimental data used [a,b]

Compound [reference]	Number of data points	Reduced temperature range	Normal boiling point temperature (K) [reference]	Critical point temperature (K) [reference]	Vapour thermal conductivity at normal boiling point (W m⁻¹ K⁻¹) [reference]	Conductivity at critical point (W m⁻¹ K⁻¹) [reference]
Ammonia [46]	25	0.591–1.000	240.0 [43]	405.5 [46]	0.01927 [46]	0.2425 [4]
Argon [43]	15	0.562–1.000	87.29 [44]	151.2 [44]	0.00576 [43]	0.025 [43]
Bromine [43]	31	0.514–1.000	331.9 [4]	584.0 [4]	0.00534 [43]	0.0280 [43]
n-Butane [47]	46	0.641–1.000	272.7 [4]	425.3 [4]	0.01406 [47]	0.05192 [47]
Chlorine [43]	24	0.480–1.000	238.7 [4]	417.2 [4]	0.00681 [43]	0.040 [43]
Ethylene [16]	29	0.538–1.000	170.0 [43]	282.4 [16]	0.00744 [16]	0.07274 [16]
Fluorine [43]	12	0.347–1.000	85.0 [4]	144.0 [4]	0.0070 [43]	0.040 [43]
Iodine [17]	24	0.568–1.000	457.5 [4]	785.0 [4]	0.00510 [17]	0.02650 [17]
Krypton [43]	19	0.571–1.000	120.0 [4]	210.0 [4]	0.00406 [43]	0.021 [43]
Methane [15]	20	0.585–1.000	112.0 [4]	190.6 [4]	0.01239 [15]	0.06615 [15]
Neon [43]	20	0.607–1.000	27.09 [4]	44.5 [4]	0.00784 [43]	0.033 [43]
Nitric oxide [17]	25	0.568–1.000	121.4 [4]	180.0 [4]	0.01140 [17]	0.04949 [17]
Nitrogen [17]	25	0.568–1.000	77.4 [4]	126.2 [4]	0.00725 [17]	0.03579 [17]
Oxygen [43]	14	0.582–1.000	90.0 [43]	154.7 [43]	0.0081 [43]	0.041 [43]
Radon [43]	20	0.530–1.000	211.2 [45]	377.2 [45]	0.00273 [43]	0.0138 [43]
Xenon [14]	19	0.500–1.000	165.0 [4]	289.8 [4]	0.00337 [14]	0.01683 [14]
Water [48]	44	0.285–1.000	373.15 [48]	647.3 [48]	0.02509 [48]	3.65178 [48]

[a] Molecular weight taken from reference [49].

[b] Most of thermal conductivity of saturated vapour values have been obtained by extrapolation of measurements in the single phase with known uncertainties cited in references given.

Table 2

Coefficients for use in equations (4) and (5)

Coefficients for use in eqn. (4)			
Compound	m	k	b
Ammonia	0.5826	0.1194	0.9252
Argon	0.6991	0.0368	0.5096
Bromine	0.6002	0.1149	0.8637
n-Butane	0.8871	0.1207	0.2959
Chlorine	0.7247	0.0549	0.4411
Ethylene	0.8232	0.0057	0.2268
Fluorine	0.6649	0.0774	0.6133
Iodine	0.6322	0.0627	0.6944
Krypton	0.7026	0.0724	0.5344
Methane	0.6780	0.0222	0.5314
Neon	0.6668	0.0508	0.5890
Nitric oxide	0.5268	0.1044	1.0944
Nitrogen	0.5860	0.0774	0.8278
Oxygen	0.6900	0.0862	0.5841
Radon	0.7089	0.0527	0.5114
Water	0.6086	0.1122	0.7827
Xenon	0.6809	0.0647	0.5491

Coefficients for use in eqn. (4) obtained from eqn. (5)—MW expansion of halogen and inert gas families.

Compound family	Coefficient expansion of eqn. (5)		
	m	k	b
Halogens	0.6555	-1.6288×10^{-6} $(MW - 80.15)^2 + 0.1009$	-2.6194×10^{-6} $(MW - 113.6)^2 + 0.6788$
Inert gases	0.7058	-1.9289×10^{-6} $(MW - 144.1)^2 + 0.064913$	-1.1373×10^{-8} $(MW - 3422.0)^2 + 0.3659$

constant for the family considered and is independent of the compound molecular weight.

The validity of the presented correlation was successfully tested by comparing the RMS % error values of this work (Table 3) with the RMS % error values as obtained using Eucken [20], modified Eucken [21] and hard sphere [4] equations (see Table 4 for data used) for the low pressure range, and then extending each one of these methods to high pressures using Stiel–Thodos [22] relations.

DISCUSSION AND RESULTS

The simple corresponding states theory [23–25] for thermal conductivity of pure fluids assumes the following conditions: the molecules interact with

Table 3

Comparison of results in RMS % error [a]

Compound	Proposed method		Other methods		
	Eqn. (4)	Eqn. (5)	Stiel–Thodos adjusted Eucken equation [20,22]	Stiel–Thodos adjusted modified Eucken equation [21,22]	Stiel–Thodos adjusted hard sphere equation [4,22]
Ammonia	2.27	–	–	–	–
Argon	1.09	2.01	11.37	11.37	14.59
Bromine	1.19	1.80	–	–	–
Chlorine	1.90	3.68	8.76	5.13	–
Ethylene	1.31	–	–	–	–
Fluorine	2.20	3.15	4.32	7.58	–
Iodine	2.54	2.23	–	–	–
Krypton	1.01	1.46	1.90	1.90	3.67
Methane	2.36	–	–	–	–
n-Butane	1.36	–	–	–	–
Neon	1.19	1.25	6.27	6.23	8.49
Nitric oxide	0.59	–	–	–	–
Nitrogen	7.27	–	–	–	–
Oxygen	1.17	–	–	–	–
Radon	1.38	1.39	–	–	–
Water	35.53	–	3524.57 [b]	3525.16 [b]	–
Xenon	1.59	1.80	5.81	5.78	7.49

[a] Root-mean-square (RMS) percent error is given by

$$\left[\frac{\displaystyle\sum_{i=1}^{n} (\text{exp.} - \text{calc.}/\text{exp.})^2}{\text{Number of points, } N} \right]^{1/2} \times 100$$

[b] These methods fail for water in the vicinity of the critical point; in contrast, the proposed method yields reasonable results.

spherically symmetric two-parameter potential; molecular internal degrees of freedom do not contribute to energy transport; and the molecular translational degree of freedom is treated classically. In general [3,23,26–28], these conditions are met in the cases of the dilute monoatomic gases.

For polyatomic fluids at low densities, internal degrees of freedom contribute extensively to the thermal conductivity, and therefore, the deviations from the results predicted by the simple corresponding states theory [25,29] are large, even for conformal, chemically related substances. These deviations may be attributed to the actual [3,4] process of energy transfer in polyatomic molecules. A rigorous treatment to predict thermal conductivity of polyatomic fluids would require, therefore, a comprehensive knowledge of the separate and interactive behaviour of translational, rotational and vibra-

Table 4

Summary of data used for Eucken, modified Eucken, hard sphere and Stiel–Thodos equation [a]

Compound	Molecular parameters		Critical state parameters			Reduced temperature range ΔT_r	Coefficients for heat capacity equation $C_p = A + BT + CT^2 + DT^3$ (cal g^{-1} mol^{-1} K^{-1})			
	ϵ/k (K)	σ (Å)	Pressure (atm)	Compressibility factor	Density (g mol cm^{-3})		A	B	C	D
Argon	93.9	3.542	48.1	0.291	0.01335	0.562–1.000	4.969	-7.670×10^{-5}	1.234×10^{-8}	0.0
Chlorine	–	–	76.0	0.275	0.00808	0.647–1.000	6.432	8.082×10^{-3}	-9.241×10^{-6}	3.695×10^{-9}
Fluorine	–	–	51.5	0.288	0.01405	0.694–1.000	5.545	8.734×10^{-3}	8.269×10^{-6}	2.876×10^{-9}
Krypton	178.9	3.655	54.3	0.288	0.01096	0.571–1.000	4.967975	0.0	0.0	0.0
Neon	32.8	2.820	27.2	0.311	0.02401	0.607–1.000	4.967975	0.0	0.0	0.0
Xenon	231.0	4.047	57.6	0.286	0.00838	0.569–1.000	4.967975	0.0	0.0	0.0
Water	–	–	217.6	0.229	0.01801	0.422–1.000	7.701	4.595×10^{-4}	2.521×10^{-6}	-8.59×10^{-9}

[a] All parameters taken from Reid et al. [4]; parameters not listed here are the same as those in Table 1.
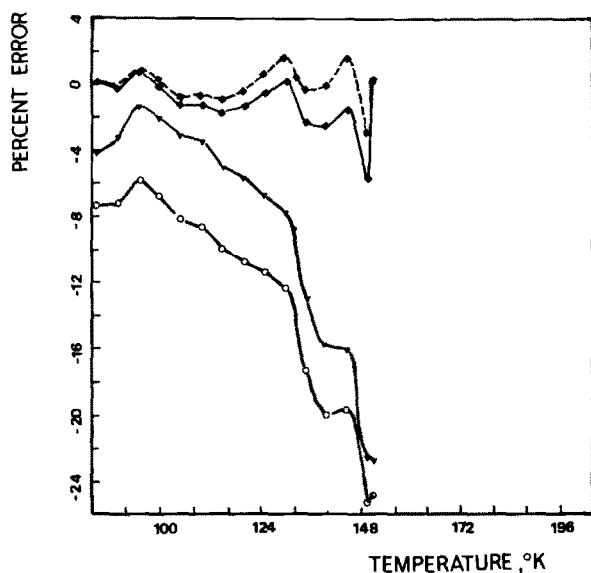
Fig. 2. Percent error in thermal conductivity vs. temperature for argon. ◆————◆, calculated using Eq. (5); ◆- - - - - -◆, calculated using Eq. (4); ▼————▼, calculated by means of Eucken and modified Eucken equations (both methods give the same result, Table 3); ○————○ calculated, hard sphere model.

tional degrees of freedom of a polyatomic molecule. For instance, Christensen and Fredenslund [25] consider these aspects of energy transfer in their recent extension of simple corresponding states theory to a generalized corresponding states model of thermal conductivity.

The introduction of the reduced coordinates, λ^* and T^* (eqns. (2) and (3)) yielding a new semi-empirical relation of the form $\lambda_s^* = f (T_s^*)$ in eqns. (4) and (5), has enabled us to estimate thermal conductivity of saturated vapour for a series of pure compounds for the entire saturated vapour–liquid equilibrium range, from the triple point to the close vicinity of the critical point, including halogen and rare gas compound families (see Tables 2 and 3 and Figs. 1 and 2).

The introduced dimensionless parameters λ^* and T^* do not refer to the magnitude and type of the intermolecular forces involved, the associated transfer rates or the description of the molecular structure of the substance. Instead, the proposed method requires knowledge of the vapour–liquid critical point and the normal boiling point temperatures, respectively, the corresponding thermal conductivities, and the molecular weight of the compound (Table 1).

To extrapolate the saturated vapour thermal conductivity values into the immediate vicinity of the critical point, we follow the earlier work [5,6,14–19] and assume that the approach to the critical point is a smooth, monotonic

continuation of the saturated liquid and vapour curves [5,6], which allows all the experimentally observed irregularities to be smoothened out and not shown [4,14–19]; consequently, the extrapolated limiting critical state thermal conductivity (see the footnote a) is a finite apparent critical state conductivity, λ_{ec} (Table 1). In effect, this thermal conductivity, λ_{ec}, introduces a useful empirical point of reference [4,14–19,30] in the proposed semi-empirical method (eqns. (4) and (5)). At any time of use it should be remembered that this extrapolated λ_{ec} parameter is not the same as the "real" λ at the critical point. The complex behaviour of thermal conductivity at the critical point has been discussed by Sengers and others [12,30–42], where, for instance, the divergence of λ for CO_2 in the immediate neighbourhood of the critical point has been studied in detail.

Table 3 compares the results expressed in terms of RMS % error values between the proposed method, using coefficients obtained from eqn. (4), coefficients from molar weight expansion (eqn. (5)) and the Eucken [20], modified Eucken [21] and hard sphere [4] equations for halogens, rare gases and a set of selected substances. Because the methods listed are low pressure correlations, these three test equations were corrected for pressure by means of the Stiel–Thodos relation [22]. Table 3 shows that the proposed method has the smallest RMS % error values among all the test equations selected. Figure 2 illustrates this graphically by giving the plot of RMS % error against temperature for argon vapour. The proposed method applies equally well to rare gases, halogens, hydrocarbons and to highly dipolar compounds, such as ammonia. For the proposed method and the other test methods used, the largest error is for water.

CONCLUSION

A semi-empirical correlation method has been developed which permits the estimation of the saturated vapour state thermal conductivity along the entire saturated vapour–liquid equilibrium curve, from the triple point to the critical point. The characteristic constants of this correlation, k and b for eqns. (4) and (5), have been obtained not only for individual compounds, but also, using a molecular weight expansion, for members of their compound family.

The range of application of the proposed method can be extended to include other compounds, compound families and compound mixtures in saturated and unsaturated states.

The results obtained and comparisons made (see Figs. 1 and 2, and Table 3) support the proposed methods.

ACKNOWLEDGEMENTS

NOMENCLATURE

A, B, C, D	coefficients in constant pressure ideal gas heat capacity equation: $C_p = A + BT + CT^2 + DT^3$
b, m, k	characteristic coefficients of pure compound, see eqn. (4)
C_p	specific heat at any temperature
$g(T_s)$	arbitrary function of temperature
$h(P_s)$	arbitrary function of pressure
k	Boltzmann's constant
MW	molecular weight
N	number of data points
P	pressure
$P(1), P(2), P(3)$	coefficients in eqn. (5)
t	temperature at any state of the saturated vapour–liquid equilibrium curve
T^*	reduced temperature
T_{NB}, T_c	normal boiling temperature, critical temperature (K) respectively
X	arbitrary (running) variable in eqn. (5)

Subscripts

c	critical point
ec	equivalent at the critical point
NB	normal boiling point
P	constant pressure
s	saturated state

Superscripts

*	reduced coordinates

Greek letters

λ	thermal conductivity
ϵ	potential energy (ergs)
σ	collision diameter (Å)

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