Thermal Conductivities of Organic Liquids—A New Correlation

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A new equation for predicting the thermal conductivities of organic liquids using dimensionless analysis is given. The equation

$$\frac{kV_m}{C_p\Delta H_v^{1/2}\sigma} = 5.6 \times 10^{-3}(M)^{1.26}$$

correlates 51 different liquids tested within 11% average error and 17% standard deviation. A comparison of the proposed equation with the available correlations and its application to some industrially important liquids show that this equation can be safely used to calculate the thermal conductivities at 20° C. and 1 atm. pressure for organic liquids of known molecular weight. C_p and ΔH_v—the only two parameters for which experimental values must be known for making use of this equation—can be calculated using other well known correlations. The proposed equation is not applicable to inorganic liquids.

THERMAL CONDUCTIVITY of liquids is frequently needed for heat transfer calculations. Experimental values of this fundamental physical property are generally rare because of experimental difficulties. A recent review (*18*) on the thermal conductivity of liquids and gases brings out this fact clearly. Many semiempirical methods are available for the prediction of thermal conductivities of liquids. In recent years, distinct theoretical advances (*16, 18*) have been made in the problem of calculating the thermal conductivity of liquids. However, the end result even for a simple liquid is far from satisfactory (*18*). The existence of many variables, of which thermal conductivity appears to be a function, has made its prediction difficult. There are at least nine methods (*3, 5, 8, 19, 23, 27, 30, 32*) available for the prediction of this property. This work describes a method of evolving a new equation through dimensionless analysis by taking all the consistent variables in the above cited nine correlations. This new equation should throw some light on the molecular heat conduction.

So far, the influence of molecular weight on the thermal conductivity of liquids is not clearly understood. A plot of k *vs.* M for a series of compounds (*8*) of various types showed a succession of sharp minima and maxima, indicating that something more than the molecular weight is involved. Even with a homologous series such as normal paraffins, there is no consistent trend of conductivity with molecular weight. In this work, the molecular weight was plotted against a dimensionless function containing the thermal conductivity. Previous work from this department (*24*) reported another similar group containing the

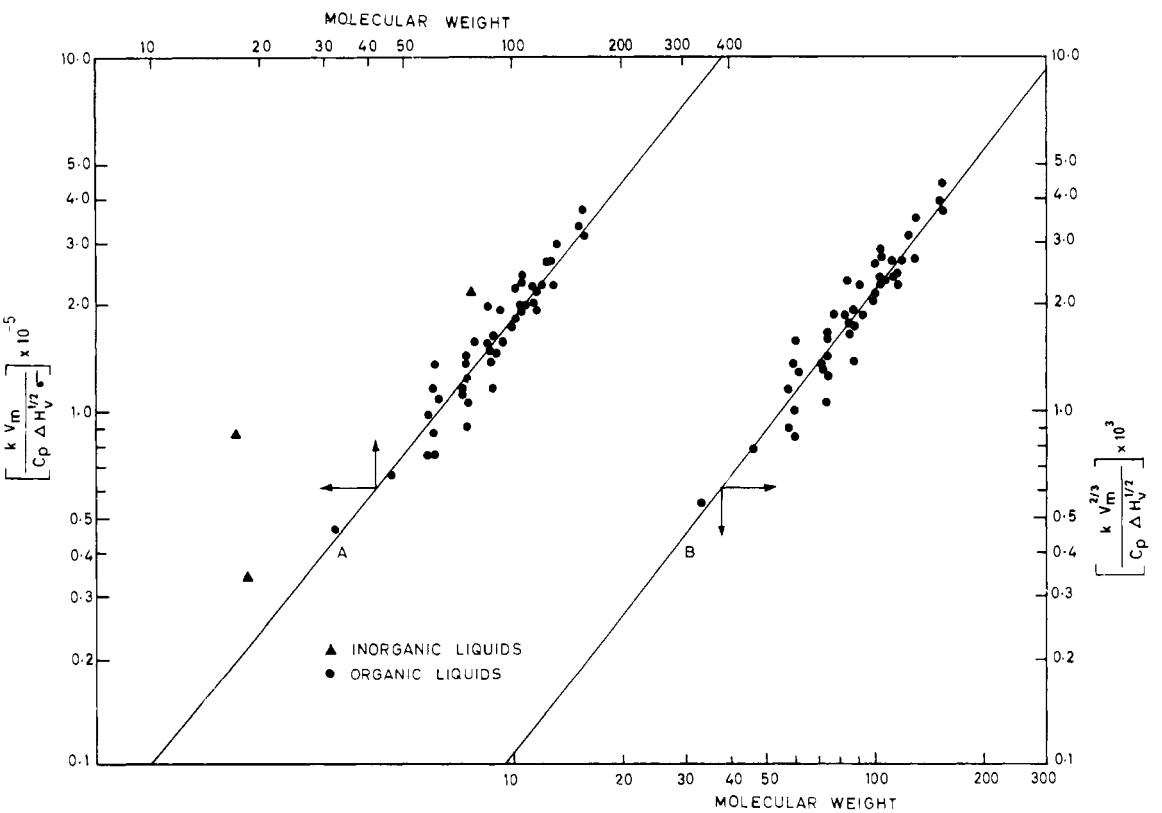

Figure 1. Correlation of thermal conductivity of liquids
A. Plot of Equation 2
B. Plot of Equation 2 eliminating σ

Table I. Relationship of New Dimensionless Number, Containing the Thermal Conductivity, with Molecular Weight

Organic Liquids	M	V_m	σ, A	C_p	ΔH_v	$k \times 10^5$	$\frac{kV_m}{C_p \Delta H_v^{1/2} \sigma} 10^{-5}$	$\frac{5.60 \times 10^{-3}}{(M)^{1.26}}$	% Error
Carbon tetrachloride	153.8	101.2[a]	5.498	0.201 (*21*)	46.50 (*25*)	0.247 (*25*)	3.321	3.182	−4.15
Chloroform	119.4	83.3[a]	5.153	0.234[b] (*21*)	59.00 (*21*)	0.246 (*25*)	2.212	2.080	+5.95
Methylene chloride	84.9	65.4[a]	4.754	0.287	78.60 (*14*)	0.368 (*25*)	1.990	1.520	−23.60
Nitromethane	61.1	58.1[a]	4.570	0.412 (*12*)	135.0 (*21*)	0.510 (*27*)	1.355	0.972	−28.27
Methanol	32.0	37.0[a]	3.932	0.601 (*21*)	262.8 (*21*)	0.483[c] (*25*)	0.468	0.436	−6.85
Trichloroethylene	131.4	98.1[a]	5.443	0.223 (*21*)	57.24 (*21*)	0.278	2.970	2.660	−10.40
Acetic acid	60.0	63.8[a]	4.716	0.488 (*4*)	96.75 (*21*)	0.411 (*21*)	1.158	0.962	−16.90
Ethyl iodide	155.9	85.1[a]	5.189	0.169	45.60 (*14*)	0.259[d] (*11*)	3.721	3.240	−12.90
Ethyl alcohol	46.0	59.2[a]	4.597	0.569 (*12*)	204.3 (*21*)	0.421[e] (*27*)	0.667	0.685	+2.70
Ethylene glycol	62.0	66.6[a]	4.783	0.574 (*21*)	191.1 (*21*)	0.624[e] (*27*)	1.095	1.020	−6.85
Diethyl ketone	86.1	118.4[a]	5.794	0.555 (*12*)	90.78 (*21*)	0.362 (*29*)	1.397	1.510	+8.10
n-Pentane	72.1	118.4[a]	8.794	0.558 (*4*)	85.40 (*14*)	0.286[f] (*14*)	1.120	1.235	+10.00
Acetone	58.0	74.0[a]	4.954	0.517 (*28*)	124.5 (*21*)	0.386 (*25*)	0.979	0.940	−4.00
Allyl alcohol	58.0	74.0[a]	4.954	0.665 (*21*)	163.4 (*21*)	0.429[b] (*21*)	0.756	0.940	+11.00
Bromobenzene	157.0	119.3[a]	5.808	0.231 (*21*)	57.60 (*21*)	0.266 (*25*)	3.121	3.295	+5.60
Chlorobenzene	112.5	113.9[a]	5.720	0.318 (*28*)	77.59 (*21*)	0.308 (*25*)	2.253	2.140	−4.90
Nitrobenzene	123.1	124.5[a]	5.890	0.339 (*12*)	79.08 (*21*)	0.380[g] (*14*)	2.664	2.440	−8.40
Benzene	78.1	96.0 (*15*)	5.402	0.406	94.12 (*25*)	0.353 (*25*)	1.591	1.350	−15.10
Aniline	93.1	115.3[a]	5.742	0.496 (*28*)	111.3 (*25*)	0.412 (*13*)	1.583	1.700	+7.40
Cyclohexane	84.1	118.2[a]	5.719	0.417	85.60 (*13*)	0.297 (*29*)	1.572	1.485	−5.50
Cyclohexene	82.1	110.8[a]	5.665	0.429 (*20*)	88.47 (*6*)	0.325 (*29*)	1.574	1.430	−8.60
n-Butyl acetate	116.1	149.1 (*15*)	6.257	0.457 (*12*)	73.82 (*21*)	0.327[e] (*27*)	1.982	2.240	+13.10
Ethyl *n*-butyrate	116.1	151.6[a]	6.292	0.457 (*28*)	76.02 (*26*)	0.341 (*27*)	2.055	2.240	+8.80
n-Propyl propionate	116.1	150.5 (*15*)	6.276	0.459 (*21*)	74.90 (*14*)	0.346 (*27*)	2.091	2.240	+7.20
n-Hexane	86.2	140.6[a]	6.133	0.534 (*28*)	80.05 (*1*)	0.313 (*27*)	1.502	1.510	+0.50
Toluene	92.1	118.2[a]	5.791	0.364 (*4*)	86.80 (*6*)	0.322 (*25*)	1.938	1.655	−14.60
p-Chlorotoluene	126.6	136.1[a]	6.068	0.315[h] (*21*)	73.10 (*14*)	0.320 (*17*)	2.659	2.500	−6.00
Methyl acetate	74.0	83.8 (*15*)	5.163	0.468 (*3*)	98.09 (*21*)	0.411 (*27*)	1.439	1.262	−12.
Propionic acid	74.0	85.3 (*15*)	5.193	0.473 (*4*)	98.81 (*21*)	0.390[g] (*14*)	1.363	1.262	−7.40
n-Propyl alcohol	60.1	81.4[a]	5.113	0.563 (*28*)	160.4 (*21*)	0.395 (*2*)	0.873	0.980	+12.20
Acetic anhydride	102.1	109.9 (*15*)	5.651	0.480	92.20 (*21*)	0.529 (*21*)	2.232	1.920	−13.90
Methyl ethyl ketone	72.1	96.2[a]	5.406	0.549 (*4*)	108.4 (*26*)	0.374 (*29*)	1.163	1.235	+6.15
Ethyl acetate	88.1	104.6 (*15*)	5.559	0.476 (*21*)	87.90 (*25*)	0.349 (*17*)	1.468	1.595	+7.95
Methyl propionate	88.1	106.1 (*15*)	5.586	0.459 (*21*)	87.56 (*21*)	0.371 (*27*)	1.642	1.595	−2.86
n-Butyl alcohol	74.1	103.6[a]	5.541	0.563 (*4*)	141.3 (*21*)	0.380[c] (*27*)	1.063	1.270	+19.4
Isobutyl alcohol	74.1	103.6[a]	5.541	0.603 (*4*)	138.1 (*21*)	0.342 (*27*)	0.904	1.270	+40.5
Ethyl propionate	102.1	128.1 (*15*)	5.948	0.457 (*21*)	80.08 (*21*)	0.351 (*27*)	1.843	1.920	+4.20
n-Propyl acetate	102.1	126.7 (*15*)	5.927	0.459 (*28*)	80.27 (*21*)	0.348 (*27*)	1.807	1.920	+6.25
Isoamyl alcohol	88.1	125.8[a]	5.912	0.549 (*4*)	119.8 (*21*)	0.364[b] (*21*)	1.172	1.595	+36.00
Methyl aniline	107.1	137.5[i]	6.088	0.512 (*21*)	95.56 (*21*)	0.442	1.991	2.020	+0.15
n-Heptane	100.2	162.8[a]	6.444	0.526 (*20*)	75.60 (*1*)	0.317 (*27*)	1.741	1.820	+4.60
n-Heptyl alcohol	116.2	170.2[a]	6.539	0.505 (*12*)	104.9 (*21*)	0.384 (*27*)	1.921	2.240	+16.60
Ethyl benzene	106.1	140.4[a]	6.131	0.402 (*12*)	81.00 (*21*)	0.316 (*25*)	2.000	2.050	+2.50
o-Xylene	106.1	140.4[a]	6.131	0.419 (*22*)	82.90 (25)	0.321 (*25*)	1.925	2.050	+6.25
m-Xylene	106.1	140.4[a]	6.131	0.387 (*14*)	82.00 (*25*)	0.376 (*21*)	2.436	2.050	−16.00
p-Xylene	106.1	140.4[a]	6.131	0.406 (*28*)	81.20 (*14*)	0.370	2.318	2.050	−11.60

n-Octane	114.2	185.0[a]	6.724	0.517 (*20*)	72.00 (*1*)	0.326 (*27*)	2.024	2.150	+6.45
n-Octyl alcohol	130.2	192.4[a]	6.812	0.499 (*12*)	97.47 (*21*)	0.397 (*27*)	2.273	2.560	+11.30
Mesitylene	120.2	162.6[a]	6.440	0.412 (*31*)	77.60 (*6*)	0.325	2.256	2.360	+4.60
Ether	74.1	107.2[a]	5.605	0.538 (*21*)	83.85 (*21*)	0.310 (*25*)	1.203	1.270	+5.80
Isopropyl alcohol	60.1	81.6[a]	5.118	0.602 (*4*)	159.4 (*21*)	0.349 (*27*)	0.728	0.980	+34.00
							Average deviation		10.7%
							Standard deviation		16.7%

The values of k and C_p are at 20° C. and the values of ΔH_v and V_m are at normal boiling point except as noted in the following cases: [a] calculated by using Le Bas additive method, [b] 30.0° C., [c] Extrapolated to 20.0° C., [d] 18.0° C., [e] 36.0° C., [f] 14.0°C., [g] 12.0° C., [h] 0° C.

Table II. Comparison of Predicted Thermal Conductivity By Different Methods

						Thermal Conductivity							
Liquids	M	V_m	σ, A.	C_p	ΔH_v	Exptl.	This work, Eqn. 3	% Error	Sakiadis and Coates	% Error	Weber	% Error	Palmer	% Error
o-Xylene	106.1	140.4[a]	6.131	0.419 (*22*)	82.90 (*25*)	0.321 (*25*)	0.342	+6.45	0.251	−22.0	0.268	−17.0	0.334	+7.2
Ethyl iodide[b]	155.9	85.1[a]	5.189	0.169	45.60 (*21*)	0.204[b] (*25*)	0.226	−11.2	0.188	−7.8	0.264	+29.0	0.336	+65.0
Carbon tetrachloride	153.8	101.2[a]	5.498	0.201 (*21*)	46.50 (*21*)	0.247 (*17*)	0.237	−4.0	0.177[b]	−28.2	0.255	+3.2	0.328	+33.0
Ethyl benzene	106.1	140.4[a]	6.131	0.402 (*12*)	81.00 (*21*)	0.316 (*25*)	0.324	+2.5	0.335	+5.4	0.261	+17.0	0.328	+3.8
m-Cresol	108.1	125.6[a]	5.900	0.441 (*21*)	100.6 (*21*)	0.359 (*25*)	0.464	+29.3	0.540	+50.0	0.402	+12.0	0.254[c]	−29.3
Iodobenzene	204.0	130.0 (*25*)	5.977	0.186 (*28*)	46.80 (*25*)	0.244 (*25*)	0.269	+10.0	0.219	−10.0	0.253	+3.7	0.323	+32.0
Ethyl alcohol[b]	46.0	59.2[a]	4.597	0.569 (*12*)	204.3 (*21*)	0.412[b] (*28*)	0.433	+2.9	0.433	+5.0	0.452	+9.7	0.445	+8.0
Bromobenzene	157.0	119.3[a]	5.808	0.231 (*21*)	57.6 (*21*)	0.267 (*25*)	0.281	+5.25	0.269	+0.7	0.269	+0.7	0.339	+27.0

The values of C_p and k are at 20° C. except as follows: [a] calculated by using Le Bas additive method, [b] 30° C., [c] calculated.

Table III. Thermal Conductivities of Some Industrially Important Liquids

Liquids	M	V_m[a]	σ, A.	C_p	ΔH_v	Exptl.	This Work, Eq. 3	% Error
Dimethyl aniline	121.2	152.4[a]	6.302	0.410	80.8 (*21*)	0.341 (*25*)	0.355	+4.10
Glycerol	92.1	96.2[a]	5.408	0.570 (*27*)	435.9[b]	0.733 (*27*)	1.106	+33.73
n-Propyl iodide	170.0	107.1[a]	5.600	0.205 (*27*)	47.24	0.221 (*27*)	0.265	+19.90
n-Amyl alcohol	88.1	125.5[a]	5.900	0.560 (*27*)	120.2 (*21*)	0.369 (*27*)	0.464	+20.30
n-Amyl chloride	106.6	135.3[a]	6.057	0.440 (*27*)	87.16 [b]	0.291 (*27*)	0.368	+26.46
n-Amyl bromide	151.1	141.7[a]	6.152	0.295 (*27*)	48.26 (*21*)	0.262 (*27*)	0.276	+5.30
n-Decane	142.3	229.4[a]	7.200	0.493	60.20 (*14*)	0.318 (*27*)	0.353	+11.00
n-Decalin	138.2	184.6[a]	13.58	0.384 (*9*)	68.25[b]	0.256[c] (*10*)	0.312	+21.88
Bicyclohexyl	166.3	228.0[a]	15.10	0.431 (*9*)	64.43[b]	0.256[c] (*10*)	0.383	+49.40
Pinane	138.2	191.1[a]	13.82	0.400 (*9*)	77.39[b]	0.244[c] (*10*)	0.338	+38.52
Freon-12	120.9	75.4[a]	4.985	0.148 (*14*)	39.96 (*14*)	0.231[d]	0.192	−16.90
Freon-21	102.9	70.4[a]	4.873	0.180 (*14*)	56.53 (*14*)	0.318[d]	0.180	−43.40
Freon-113	234.3	145.1[a]	6.201	0.213	38.00	0.238[d]	0.303	+27.30

[a] Calculated by using Le Bas additive method. [b] Calculated by using Riedel method. [c] k at 64° C. [d] 0 to 75° C.

thermal conductivity and diffusion coefficient, but the accuracy in the present work is considerably improved.

The nine available correlations indicate that the thermal conductivity is a function of heat capacity; density or molecular volume; intermolecular separation distance or, for simplicity, molecular diameter or Lennard-Jones potential constant; molecular weight; latent heat of vaporization; viscosity; freezing point; and the compressibility of the liquids. Gas constants and other similar constants are omitted. As the first five parameters are cited by almost all the correlators as a first approximation, the thermal conductivity of liquids is assumed, in this work, to be influenced by the above first five parameters.

Combining all of these parameters gives a dimensionless equation of the form

$$M = f(k, V_m, C_p, \Delta H_v, \sigma) \tag{1}$$

By use of dimensionless analysis, a dimensionally consistent equation is obtained for molecular weight, from which the thermal conductivity of liquids can be calculated. As the molecular weight, molecular volume, and the Lennard-Jones potential constant having the dimension of length are all fixed physical properties, only the heat capacity and the latent heat of vaporization at boiling point need to be known to arrive at the values of the thermal conductivity of liquids. In cases where the experimental values of heat capacity and latent heat of vaporization are not readily available, the correlation of Sakiadis and Coates (*28*) for heat capacity and the correlation of Riedel (*26*) for latent heat of vaporization may be used. For the calculation of critical properties, Eduljee's (*7*, *8*) correlations may be used.

$$M = f\left[\frac{kV_m}{C_p\Delta H_v^{1/2}\sigma}\right] \tag{2}$$

ORGANIC LIQUIDS

Experimental data have been collected for 51 organic liquids whose molecular weight ranged between 30 and 160. The right hand side function of Equation 2 was plotted against molecular weight, on logarithmic coordinates (Table I). A statistical average gave a straight line (line *A*, Figure 1) whose equation is

$$\frac{kV_m}{C_p\Delta H_v^{1/2}\sigma} = 5.6 \times 10^{-3}(M)^{1.26} \tag{3}$$

Equation 3 gave an average error of 11.0%, and the standard deviation for this equation is 17.0%. Without sacrificing the accuracy, Equation 3 is simplified further using the relationship $\sigma = 1.18V_m^{1/3}$. Eliminating σ from Equation 2, one obtains a relation for molecular weight

$$M \propto \frac{kV_m^{2/3}}{C_p\Delta H_v^{1/2}}$$

A similar plot (line *B*, Figure 1) gives a linear equation

$$\frac{kV_m^{2/3}}{C_p\Delta H_v^{1/2}} = 5.4 \times 10^{-3}(M)^{1.30} \tag{4}$$

The average error for this equation is 12.0%, and the standard deviation is 18.0%.

Of the nine correlations mentioned earlier, the Sakiadis and Coates (*27*) method is the best. For the liquids tested by Reid and Sherwood (*25*), this method gives an average error of 16 to 19%, and the standard deviation is 26.0% (calculated by the authors). However, the error attributed to the Sakiadis and Coates value for acetic acid by Reid and Sherwood (*25*) seems to be exaggerated. Even after allowing for this fact, the authors believe that Equation 3 or 4 should be favorable for computing the thermal conductivity of organic liquids.

The usefulness of Equation 3 is further brought out in Table II. The thermal conductivities calculated by Equation 3 for about eight typical organic liquids are compared with the values obtained by other correlations on thermal conductivity. Equation 3 definitely gives values nearer to the experimental values. Table III gives the thermal conductivity calculated by the method outlined in this work for some industrially important liquids.

INORGANIC LIQUIDS

The validity of Equation 2 for inorganic liquids was tested for water, carbon disulfide, ammonia, and mercury, and the results except for mercury are included in line *A* of Figure 1. Equations 3 and 4 are not recommended to calculate the thermal conductivity of inorganic liquids.

NOMENCLATURE

k = thermal conductivity of liquids, $MLT^{-3}\theta^{-1}$
V_m = molecular volume, L^3M^{-1}
C_p = heat capacity, $L^2T^{-2}\theta^{-1}$
ΔH_v = latent heat of vaporization, L^2T^{-2}
σ = Lennard-Jones potential constant, L
M = molecular weight

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