and the void fraction of the bed were plotted against the corresponding Reynolds number, as shown in Figure 4. Only the data of studies in which surface temperatures were measured directly were utilized and include j_h values for packed, expanded, and distended beds. No experimental heat transfer factors are presently available for fluidized beds. Again considerable scatter is noted at low Reynolds numbers, due to backmixing effects. The deviations of the j_h values reported by De Acetis and Thodos (*3*) can be attributed to the significant conduction and radiation effects which were not accounted for in that study. The best relationship, which is limited to the region $N_{Re} > 20$ for which substantial experimental data are available, may be expressed analytically as follows:

$$\epsilon j_h = 0.0108 + \frac{0.929}{N_{Re}^{0.68} - 0.483} \quad \text{for } N_{Re} > 20 \qquad (2)$$

Dividing Equation (2) by Equation (1) for the region $N_{Re} > 20$ where both equations apply, one obtains $\frac{\epsilon j_h}{\epsilon j_d} = \frac{j_h}{j_d} = 1.076$, which is consistent with the previously reported values (*7*, *11*).

Evnochides and Thodos (*4*) have established mass and heat transfer factors for the flow of air past a single sphere. For this case the void fraction is equal to unity. Transfer factors calculated from Equations (*1*) and (*2*) with $\epsilon = 1$ are consistent with the corresponding experimental values obtained by Evnochides and Thodos for $N_{Re} \approx 2{,}000$, which is the lowest Reynolds number considered in their study and the highest value utilized in the present investigation. Therefore Equations (*1*) and (*2*) do not have the disadvantage of the previous correlations which utilized the factor $(1 - \epsilon)$ and thus could not be extended to include the limiting case of flow past a single sphere.

Values of mass and heat transfer factors calculated with Equations (*1*) and (*2*) were compared with the corresponding values obtained from experimental data. Equation (*1*) was found to reproduce 380 j_d values reported by eight investigators with an average deviation of 15.6% while Equation (*2*) reproduced 168 j_h values reported by four investigators with an average deviation of 17.1%. The average deviation is defined as the ratio of the difference between the value reported in the literature and calculated to the value reported in the literature. In these comparisons j factors were obtained from experimental data from several sources which appear to be inconsistent and in which experimental errors are indicated. Thus these average deviations are quite probably higher than those which might have resulted if these questionable values had been eliminated in the comparisons.

NOTATION

c_p = heat capacity, B.t.u./lb. °F.
c_{lf} = concentration of nontransferable component, lb. moles/ cu. ft.
D_p = particle diameter, ft.
D_l = diffusivity of transferable component in liquid phase, sq.ft./hr.
D_v = diffusivity of transferable component in gas phase, sq.ft./hr.
G = superficial mass velocity of flowing gas, lb./hr. sq.ft.
h = heat transfer coefficient, B.t.u./sq.ft. °F.
j_d = mass transfer factor, $\frac{k_g p_{gf}}{G/M} \left(\frac{\mu}{\rho D_v}\right)_f^{2/3}$; $\frac{k_l c_{lf}}{L/M} \left(\frac{\mu}{\rho D_l}\right)_f^{2/3}$
j_h = heat transfer factor $\frac{h}{c_p G} \left(\frac{c_p \mu}{k}\right)_f^{2/3}$
k = thermal conductivity, B.t.u./hr. ft. °F.
k_g = mass transfer coefficient for gas film, lb. moles/hr. sq.ft. atm.
k_l = mass transfer coefficient for liquid film, lb. moles/hr. sq.ft. $\frac{\text{lb. mole}}{\text{cu.ft.}}$
L = superficial mass velocity of flowing liquid, lb/hr. sq.ft.
M = molecular weight of flowing stream, lb./lb. mole
N_{Re} = Reynolds number D_pG/μ
p_{gf} = partial pressure of nontransferable component in gas film, atm
ϵ = void fraction of bed
μ = viscosity, lb./hr.ft.
ρ = density, lb./cu.ft.

LITERATURE CITED

1. Baumeister, B. E., and C. O. Bennett, *A.I.Ch.E. Journal*, **4**, 69 (1958).
2. Chu, J. C., James Kalil, and W. A. Wetteroth, *Chem. Eng. Progr.*, **49**, 141 (1953).
3. De Acetis, James, and George Thodos, *Ind. Eng. Chem.*, **52**, 1003 (1960).
4. Evnochides, Spyros, and George Thodos, *A.I.Ch.E. Journal*, **7**, 78 (1961).
5. Gaffney, B. J., and T. B. Drew, *Ind. Eng. Chem.*, **42**, 1120 (1950).
6. Gamson, B. W., *Chem. Eng. Progr.*, **47**, 19 (1951).
7. ———, George Thodos, and O. A. Hougen, *Trans. Am. Inst. Chem. Engrs.*, **39**, 1 (1943).
8. Glaser, M. B., and George Thodos, *A.I.Ch.E. Journal*, **4**, 63 (1958).
9. Hobson, Merk, and George Thodos, *Chem. Eng. Progr.*, **45**, 517 (1949).
10. *Ibid.*, **47**, 370 (1951).
11. McConnachie, J. T. L., M.S. thesis, Northwestern Univ., Evanston, Illinois (1961).
12. McCune, L. K., and R. H. Wilhelm, *Ind. Eng. Chem.*, **41**, 1124 (1949).

Manuscript received June 19, 1961; revision received September 29, 1961; paper accepted October 5, 1961.

Thermal Conductivity of Nonassociated Liquids

A. A. BONDI
Shell Development Company, Emeryville, California

The thermal conductivity of liquids composed of nonionized molecules covers a comparatively small range of numerical values, the largest and the smallest known values differing by less than a factor of 10. Yet heat transfer coefficients are sufficiently sensitive to the magnitude of the thermal conductivity (which is very difficult to measure) to make a fairly accurate estimate of it worthwhile if it can be had with comparatively little effort.

The specific objective of the present work is to estimate the thermal conductivity of molecular liquids from only the molecular structure. Allowance was made for improvement of prediction through the availability of density data however.

The only correlating parameters were to be the van der Waals volume, the energy of vaporization, and the number of external degrees of freedom, for all of which simple molecular structure correlations had been developed previously (*5*, *6*). Appropriate combinations of these properties lead to what appears to be an acceptable correlation of thermal conductivity data.

This report treats only liquids composed of nonpolar molecules, or of polar molecules without hydrogen bonding groups (hydroxyl, carboxyl, or amide). The transport properties of these strongly associating compounds will be discussed in a separate paper.

GENERAL PRINCIPLES

Molecular theories of thermal conductivity can be divided into two groups: the rigorous statistical mechanical theories of transport processes by Kirkwood and his school (*34*) and by Collins and his collaborators (*13*), and the less ambitious attempts to represent thermal conductivity in terms of free volume theories of the liquid state (*21*, *24*). The rigorous theories have so far appeared only as complicated integro-differential equations giving the thermal conductivity as a function of the disturbance of the radial distribution function by the temperature gradient and containing the expected molecular properties m, ϵ, and C_V. The very crude approximations made in the process of getting some sort of numerical answer out of the equations are somewhat opaque, and the results, purporting to give the thermal conductivity as a function of thermodynamic variables (*11*) or of diffusion constant and viscosity (*32*), do not even look plausible, at least to the author.

The free volume theories of thermal conductivity yield more easily intelligible results. A typical form is that by Horrocks and McLaughlin (*19*) who obtain for the dominant term

$$\lambda \doteq \left[\frac{\epsilon}{\pi^2 r_o^2 m}\left\{11C_{14}\left(\frac{r_o}{a}\right)^{14} - 5C_8\left(\frac{r_o}{a}\right)^8\right\}\right]^{1/2} \frac{\Psi C_V}{a}\sqrt{2}\left(1-\frac{n_h}{N_A}\right) \qquad (1)$$

where n_h = number of holes per mole.* As $n_h/N_A << 1$, the last term in parentheses $\approx$ 1. Rearrangement of the equation to separate molecular properties and state variables yields

$$\frac{\lambda \cdot r_o^2}{C_V}\left(\frac{m}{\epsilon}\right)^{1/2} = \frac{\sqrt{2}\,\Psi}{\pi}$$

$$[A(\rho^*)^{16/3} - B(\rho^*)^{10/3}]^{1/2} \qquad (2)$$

where A and B are constants of similar order, approximately $A \sim 2B$. It is generally assumed that the components of C_V active in thermal conductivity are those due to the external degrees of freedom of a molecule, for example $3R$ for rigid nonlinear polyatomic molecules. One sees that λ should increase with the reduced density ρ^*, as is indeed observed, at least at atmospheric and at moderately high pressures. The equation does not contain temperature explicitly and therefore does not represent the well-known experimental observation that λ increases with increasing temperature at very high pressures (> 3,000 atm.). This failing is shown by all thermal conductivity equations derived from free volume theories.

For simple substances ρ^* is a unique function of the reduced temperature $T^* (= kT/\epsilon)$. Then one can also write $(\lambda r_o^2/C_V)(m/\epsilon)^{1/2} = f(T^*)$. A noteworthy feature of Equation (2) is that the left-hand side, the collection of molecular properties, is virtually identical with that derived by Owens and Thodos (*27*) and by Helfand and Rice (*17*) from dimensional analysis if one sets C_V = 3R.

APPLICATION TO POLYATOMIC MOLECULES

The properties r_o and ϵ are uniquely determined only in monatomic substances and are generally derived from the kinetic theory analysis of p-v-t properties, the viscosity of gases, or from the heat of sublimation and the elastic properties of crystals. The latter procedure would in princple also be useful for the comparatively nonvolatile substances, if their properties could validly be represented by assuming spherical molecules in uniform force fields.

A more general approach is to divorce oneself from any specific model and simply take the standard energy of vaporization E° described in Tables 2 and 3 as a measure of the intermolecular force (in place of ϵ) and find

TABLE 1. COMPARISON OF PROPERTIES REQUIRED TO ESTIMATE THE THERMAL CONDUCTIVITY OF A LIQUID AT TEMPERATURE T

Method	Required properties	Condition
This paper (for estimate) Equations (8), (9), Tables 2 and 3	Molecular structure	If hydrocarbon or nonassociating N, O, S, or halogen compound
This paper (for greater accuracy) Equation (3), Tables 2 and 3	Molecular structure, density (preferably at two temperatures)	Same
This paper	Density (at two temperatures), in order to obtain the reduced temperature T^*, heat of vaporization (or vapor pressure at two temperatures) in order to estimate the standard energy of vaporization $E^\circ = \Delta H_v - RT$ at the temperature when V/V_w = 1.70	If no tabulated increments are available for E° or for 3c
Weber (*31*)	Molecular weight, density (at T), specific heat of liquid (at T)	
Sakiadis and Coates (*31*)	Molecular structure, density (at T), density (at freezing point), density (at critical temperature), critical temperature, specific heat of liquid (at T)	If structural increments are available for the sound velocity
Sakiadis and Coates (*31*)	All above and sound velocity (at T)	If no structural increments are available for the sound velocity

---

* The very similar relation $\lambda = (6.96\ k/v^{2/3})(\Delta E_v/M)^{1/2}$ where v = liquid volume/molecule, ΔE_v = energy of vaporization, has been derived from a solidlike model of the liquid state by Altenburg (*1*).

TABLE 2a. STANDARD ENERGY OF VAPORIZATION INCREMENTS FOR HYDROCARBON FRAGMENTS

Type	Fragment	$E^\circ(R\cdot)$† kcal./mole	$E^\circ(R:)$** kcal./mole
Aliphatic			
saturated	Me.	1.97	1.07
	et.	3.13	2.14
	n-pr.	4.20	3.01 (1, 2)
	i-pr.	3.93	3.07 (1, 1)
	n-bu.	5.35	
	sec.-bu.	5.03	
	i-bu.	4.99	
	t-bu.	4.62	
mono unsaturated	vinyl	3.22	2.30
	n-propenyl	4.16	
	i-propenyl	4.26	
açetylenic	ethynyl	3.75	
	propynyl	4.71	
cycloaliphatic	cyclopentyl	$6.10 - 0.20 \sum_{2}^{N_B*} \frac{1}{N_B - 1}$	4.8
	cyclohexyl	$6.85 - 0.20 \sum_{2}^{N_B} \frac{1}{N_B - 1}$	5.5
cycloaliphatic	decalyl	9.60	
Aromatic			
	phenyl	$7.27 - 0.30 \sum_{2}^{N_B} \frac{1}{N_B - 1}$	$7.27 - 1.2\,(b - 1)$ $-0.3 \sum_{2}^{N_B} \frac{1}{N_B - 1}$
	naphthyl	10.65	
	anthryl	14.1	

* N_B = number of carbon atoms in alkyl chain.
† $E^\circ(R\cdot)$ refers to monoradical fragment; for example et. = ethyl.
** $E^\circ(R:)$ refers to biradical fragment; for example me. = methylene.

some suitable measure of molecular dimensions to take the place of r_o.

In this choice of dimensions one can only be guided by intuition to see that energy is transferred through oscillations in the drag of intermolecular force fields. The simplest guess might be $V_W^{1/3}$ as the appropriate measure of length. However this choice would imply that the amplitude of molecular vibrations of polyatomic molecules in liquids (or solids) increases with increasing size of the molecules. Evidence from the X-ray diffraction of crystals (*24*) and from the analysis of liquid density (*4*) suggests on the contrary that the amplitude of thermal motion of polyatomic molecules is quite unrelated to molecule size.

A better measure of the significant dimension therefore seems to be the average minimum distance (d_w) of the outer atoms of neighboring molecules in contact at 0°K. Then

$$\bar{d}_w = \frac{1}{n} \sum_{n=1}^{n=i} d_w(i)$$

where $d_w(i)$ are the van der Waals diameters of all outer atoms of a molecule. Exceptions are methyl and methylene groups for which d_w = 4.00 A° was adopted and aromatic rings for which $d_w(\mathrm{CH})$ = 3.73 A°, $d_w(\mathrm{C})$ = 3.54 A°. All other $d_w(i)$ data have been taken from reference *6*.

The results given below indicate that this choice of molecular dimension was not too poor, especially if one keeps in mind that, owing to the comparative insensitivity of $(E^\circ/M)^{1/2}$ to many composition changes, the term d^2_w carries a great deal of weight. Further refinement of the method might therefore start with a reinvestigation of the correct choice and magnitude of $\bar{d}_w$.

The author has followed the indications of previous investigations that the heat capacity contribution to energy transfer in liquids proceeds via the external degrees of freedom and should equal $3R$ for simple rigid polyatomic molecules. For these one can therefore set the reduced thermal conductivity as

$$\lambda_s{}^* = \frac{\lambda}{\lambda'} = \frac{\lambda \cdot \bar{d}_w{}^2 \cdot N_A}{R} \left(\frac{M}{JE^\circ}\right)^{1/2} = 4.69 \times 10^{19} \lambda\, d_w{}^2 \,(M/E^\circ)^{1/2} \quad (3)$$

This choice of reducing parameters leads to the convenient coincidence that λ^* ranges between 1.5 and 2.5 from the atmospheric boiling down to the melting points of most liquids. Philosophically minded people may see in the proximity of the magnitudes of the measured quantity and of the reducing parameters λ' a confirmation of the physically correct choice of λ'.

RIGID MOLECULES

The theory of Horrocks and McLaughlin (*19*), Equations (1) and (2), suggests that the reduced density $\rho^* (= V_w/V)$ should be used as an independent variable. As experimental density data are not always available for the temperature range of interest, it is more convenient to express λ^* as a function of a reduced temperature T^*. For rigid molecules for which, according to reference *6*, $3c = 6$ the reducing temperature $\theta_L = E^\circ/10R$. If density data are available, one does not have to assume $3c = 6$ but may determine the reference temperature $T(1.8)$ at which $V/V_w = 1.80$ experimentally. Then, in accordance with reference *5*, $\theta_L = T(1.8)/(0.6518)$. The reduced temperature is of course $T^* = T/\theta_L$. A plot of most available thermal conductivity data for rigid molecules, as $\lambda_s{}^*$ vs. T^*, is shown in Figure 1.

While for the few compounds whose data cover the entire temperature range of the graph a convex curvature can be discerned, a straight line

$$\lambda_R{}^* = 3.22 - 1.76\, T^* \quad (4)$$

describes the data between $T^* = 0.4$ and 0.9 within the scatter of the points. The above mentioned curvature and the very similar curvature on the plot for the rare gases, presented by Owens and Thodos (*27*), suggest that the linear relation (3) not be used for extrapolation outside the range covered by the graph.*

Detailed inspection of Figure 1 shows that the slope of the λ^* vs. T^* curves is nearly the same for all of those compounds in which the data cover more than 0.2 units in T^*. These compounds differ sufficiently in chemical composition to make very large deviations from the pattern suspect. Only the following substances fall significantly outside the ±8% average errors limit of the graph (and of most modern thermal conductivity measurements): above cyclohexane and triethylamine (perhaps also benzene); below nitrobenzene, methyl benzoate,

---

* However the thermal conductivity of propane at $T^* = 1.27$ and 1.42 ($\sim T_c$) reported by reference *23*, along the saturation line, is even slightly higher than predicted by Equation (3).

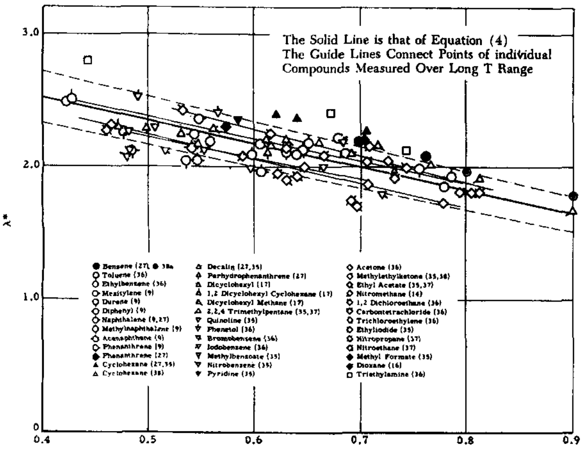


Fig. 1. Plot of λ^* vs. T^* for liquids composed of rigid molecules.

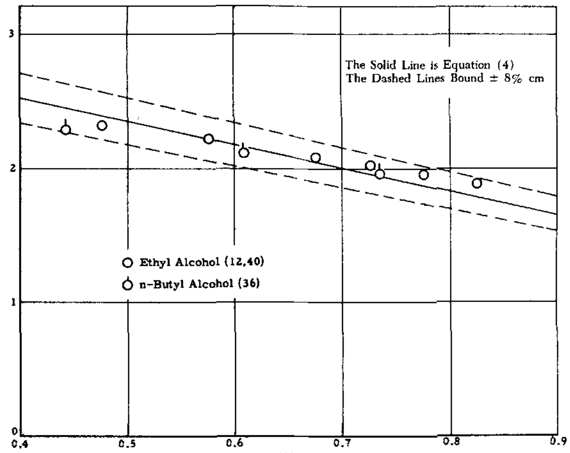


Fig. 3. Location of the monohydric alcohols and *n*-butyl alcohol data on the plot of λ^* vs. T^* of Figure 2.

and a few improbable values of naphthalene and phenanthrene, as well as the probably incorrect high temperature data for nitroethane and nitropropane. From this it appears that only the excessively high data need an explanation. It is striking that the saturated ring compounds, cyclopentane (not shown on the graph), and cyclohexane exhibit higher than average conductivities in spite of their small number of external degrees of freedom ($3c = 6 \pm 0.5$). A possible explanation is that their well-known internal motions contribute to thermal conductivity but not to density (from which $3c$ is usually calculated). No quantitative estimate of such a contribution can be made at present.

The largest deviation is that for triethylamine. A large portion of this deviation is accounted for by the somewhat larger internal mobility[*] of triethylamine ($3c = 6.7$) than that of triethyl methane ($3c = 6.1$). With the method in the following section one finds that this internal mobility accounts for about two-thirds of the observed deviation. The remaining deviation may well be experimental error.

The only discernible trend has so far been found in the two series benzene, naphthalene, phenanthrene, and cyclopentane, cyclohexane, decalin, perhydrophenanthrene, in which λ^* decreases (at constant T^*) as the molecular weight increases. Closer inspection suggested that perhaps in these comparatively rigid ring systems a better fit might be obtained by choosing $(V_w/N_A)^{1/3}$ as the linear dimension and setting

$$\lambda^* = \frac{\lambda N_A^{1/3} V_w^{2/3}}{R} \left(\frac{M}{JE^\circ} \right)^{1/2} \quad (5)$$

However calculation by means of this definition of a reduced thermal conductivity yielded a very much stronger rather than weaker dependence of λ^* on molecule size. A remedy for the very slight dependence of λ_s^* on molecule size must therefore be of a more subtle nature than has been tried so far.

A peculiar facet of the behavior of the cyclic hydrocarbons is the closeness of most methyl and ethyl derivatives to the center of the point distribution [the line corresponding to Equation (3)] regardless of how far the unbranched ring compound appears to deviate. One is therefore inclined at present to treat most observed deviations as random errors.

FLEXIBLE MOLECULES

At least two previous analyses of the thermal conductivity of liquids composed of long chain molecules have indicated that these liquids exhibit higher than predicted thermal conductivity (by whatever theory) because of the flexibility of the long chain molecules (3, 33). The present correlation is no exception. The reduced thermal conductivity λ^* of normal paraffins, long chain esters, ethers, etc. with $N_S \geq 7$ is significantly larger than that of the rigid molecules discussed in the previous section.

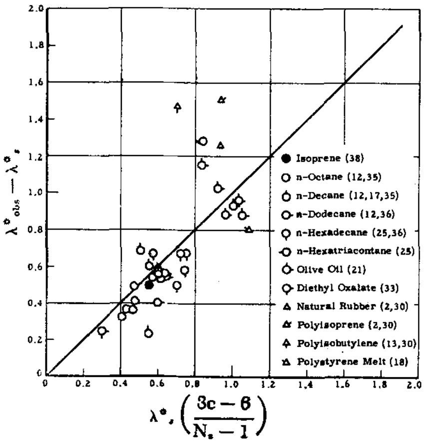


Fig. 2. Comparison of the observed with the calculated excess thermal conductivity of flexible molecules.

If one examines the difference $\lambda^* - \lambda_s^*$, one finds a rather systematic trend with the number of external degrees of freedom $3c$ discussed previously (6, 8). A fairly good representation of this relation is

$$\lambda^* - \lambda_s^* = \lambda_s^* \frac{(3c-6)}{N_S - 1},$$

$$\text{or } \lambda_F^* = \lambda_s^* \left(1 + \frac{3c-6}{N_S - 1} \right) \quad (6)$$

where λ_s^* is calculated by means of Equation (4). The accuracy with which this relation represents the data is shown in Figure 2. The meaning of Equation (6) is of course that each chain link beyond the first contributes to the thermal conductivity in proportion to its freedom to rotate.

The application of this equation to liquid polymers, such as rubber or melts of thermoplastics, is straightforward. For these substances $3c >> 6$, and therefore

$$\lambda^* - \lambda_s^* = \lambda_s^* \frac{3c}{N_S} \quad (6a)$$

The standard energy of vaporization per unit weight (E°/M) is easily obtained from the published increments for the repeat units of the polymer chain, and the dimension $\bar{d}_w$ is likewise that estimated from the atoms of the repeating unit of the chain.

There are only few data with which to compare the predictions of Equation (6*a*), and the accuracy of these experimental data is quite unknown.[*] These are shown on Figure 3.

MIXTURES

The thermal conductivity of mixtures of nonassociating liquids is gen-

---

[*] Internal rotations are counted also as external degrees of freedom (see references *8* and *31*).

[*] There is little doubt that the accuracy of the rubber data is particularly poor. Hence only the 60°C. data were used. At high temperatures an anomalous drop is apparently due to gas bubble formation.

erally somewhat lower than predicted by simple mole or weight fraction additivity. As a rule two substances with λ_A^* and λ_B^* are at the different reduced temperatures T_A^* and T_B^*. Since the interaction between species A and B, $E^*_{AB} \approx (E_A^\circ E_B^\circ)^{1/2}$, if $V_w(A) = V_w(B)$, the reduced temperature T^*_{AB} is always larger than corresponds to the arithmetic average of the mixture. If $V_w(A) \neq V_w(B)$, the interaction energy should be smaller as has been mentioned by Hudson, et al., (*20*), namely

$$E^*_{AB} \approx \frac{64(V_w(A) + V_w(B))}{[V_w^{1/3}(A) + V_w^{1/3}(B)]^6} (E^\circ_A E^\circ_B)^{1/2}$$

Hence T^*_{AB} can be larger than the reduced temperatures of the mixture components even if $T^*_A = T^*_B$, and thus $\lambda^*_{AB} < \lambda^*_A (= \lambda^*_B)$. Translation of these generalizations into detailed arithmetic for the calculation of the reduced temperature of mixtures is easiest by way of the method given in Prigogine's textbook (*29*). However to this author it appears that the results hardly warrant the laborious calculation. A more rapid if very empirical method is therefore proposed.

The approximate symmetry of the λ vs. X (= mole fraction) plot, first noted by Riedel (*35*), suggests a mixture rule of the form

$$\lambda_{12} = X_1\lambda_1 + X_2\lambda_2 - f \cdot b \cdot X_1 X_2 \quad (7)$$

The empirical constants, f and b, were found to be represented by $f = |(E_1^\circ/M_1)^{1/2} - (E_2^\circ/M_2)^{1/2}|$, and $b = 4.5 \times 10^{-5}$ if E° is expressed in calories per mole, $b = 7.0 \times 10^{-9}$ if E° is expressed in ergons per mole. If one of the mixture components is a high molecular weight (flexible chain) molecule, the mole fractions X_i should be replaced by volume fractions.

A similar equation, namely, $\lambda_{12} = w_1\lambda_1 + w_2\lambda_2 - 0.7\, w_1 w_2 |\lambda_2 - \lambda_1|$ when w_i = weight fractions, has been proposed by Philippov (*28*). However this equation does not represent the data as well as that given above, and fails to predict that $\lambda_{12} < \Sigma\, w_i \lambda_i$ even when $\lambda_1 = \lambda_2$.

COMPARISON WITH OTHER METHODS

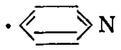
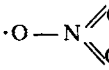
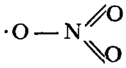
Comparison of the method proposed in this paper with published calculating procedures is possible at two levels: from the point of view of the amount of information required to carry out the calculations, and the reliability of the calculated result. The presentation in Table 1 permits a direct comparison of the amount of experimental data required. To the extent that E° and c are available from published molecular structure correlations, no other method is as simple as the present one. However even if E° and c have to be estimated from vapor pressure and density data, the present method has distinct advantages over the other methods. One advantage is that E° and c can, if necessary, be obtained from other compounds having the same functional groups as the compound under consideration; the other advantage is that E° and c, once determined, can be used for the calculation of many other physical properties.

The accuracy of the estimated results (within 8% average error) is noticeably better than that of the other published methods. Excluding hydrogen bonded compounds, the methods of Weber (*31*) and of Sakiadis and Coates (*31*) predict thermal conductivity of liquids composed of rigid molecules with average errors of 12 and 18%, respectively, and much larger errors for liquids composed of flexible molecules.

LIMITATIONS

The method of this report does not permit the calculation of the thermal conductivity of associated liquids. They will be treated in a separate paper on the effect of hydrogen bonds on transport properties in general. It has been noted that for the monohydric alcohols, ethyl alcohol, and higher, λ^* follows the curve of Equation (3) to within the same margin of error as for other liquids (Figure 3). It is also noteworthy that the reduced thermal conductivity of the polyhydric alcohols (and of water) is of the same order as that of normal liquids, but their peculiar temperature dependence is of course totally unrelated to that of the nonassociating liquids. No attempt has been made to handle the pressure dependence of thermal conductivity. To

TABLE 2b. STANDARD ENERGY OF VAPORIZATION INCREMENTS FOR FUNCTIONAL GROUPS CONTAINING NITROGEN

Type	Fragment	$E^\circ(\cdot X)$ kcal./mole
Nitrile		
aliphatic mono (R)	$\cdot C \equiv N$	$5.35 + \frac{1.00}{N_c}$
aliphatic di (α, ω)		mono — 0.40
aromatic (φ)	$\cdot CN$	5.0 (?)
Pyridine		
	$:N\cdot$ *	2.30
		8.03
Amine		
aliphatic (R_3)†	$:N\cdot$	(0.40)
aliphatic (R_2)†	$:NH$	3.26
heteroaliphatic	$:NH$	2.9
aliphatic (R)†	$\cdot NH_2$	4.33
aromatic (φ)	$\cdot NH_2$	4.24
heteroaromatic**	$:NH$	3.20
Nitro		
aliphatic primary	$\cdot NO_2$	$5.60 + \frac{1.60}{N_c}$
secondary	$\cdot NO_2$	prim — 0.3
aromatic (φ)	$\cdot NO_2$	4.87
Nitrate		
aliphatic primary		$5.20 + \frac{1.40}{N_c}$
secondary		pr — 0.2

* $X = \Delta E_v^\circ$ (cpd) − 5/6 φH.
† Good data available only for methyl derivatives; hence use X with caution.
** $X = \Delta E_v^\circ$ (cpd) − 4/5 cyclo C_5 or equivalent.

a first approximation, that is up to about 1,000 atm., this can undoubtedly be predicted from a graph of λ^* vs. ρ^*.

PROCEDURE

For easier use of the method Equation (3) is solved for λ (liquid composed of rigid molecules):

$$\lambda = \frac{R}{N_A\, d_w^{\,2}} \left(\frac{JE^\circ}{M}\right)^{1/2} \left(3.22 - \frac{8.80\, c\, RT}{E^\circ}\right) \text{cal./cm. sec. °K.} \tag{8}$$

Typical E° increments are presented in Table 2 and typical values of $3c$ are given in Table 3. For rigid molecules $3c = 6 \pm 0.5$. If the liquid is composed of flexible molecules ($3c > 7$):

$$\lambda = \frac{R}{N_A\, d_w^{\,2}} \left(\frac{JE^\circ}{M}\right)^{1/2} \left(3.22 - \frac{8.80\, c\, RT}{E^\circ}\right) \left(1 + \frac{3\,c - 6}{N_S - 1}\right) \text{cal./cm. sec. °K.} \tag{9}$$

To convert to British engineering units (British thermal units per feet hour degrees Fahrenheit) multiply λ by 241.9. This method should not be used at temperatures in excess of the atmospheric boiling point.

Example

Estimate the thermal conductivity of n-octadecane at 40°C. Table 2 yields $E^\circ = 21.40$ kcal./mole, and by means of Table 3 one finds $3c = 11.65$; $d_w = 4.00$Å, $M = 254$. Hence

$$\lambda = \frac{1.987}{0.602 \times 10^{24} \times 16 \times 10^{-16}} \left(\frac{89.5 \times 10^{10}}{2.54 \times 10^{2}}\right)^{1/2} \left(3.22 - \frac{34.2 \times 1.987 \times 313}{21{,}400}\right) \left(1 + \frac{5.65}{17}\right)$$

$$\lambda = 3.63 \times 10^{-4} \text{ cal./cm. sec. °K.}$$

This value compares favorably with the recent experimental datum, 3.64×10^{-4} cal./cm. sec. °K., reported by Powell and Challoner (*40*).

NOTATION

A = constant in Equation (2)

a = lattice parameter, cm.

B = constant in Equation (2)

b = constant in Equation (5)

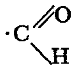
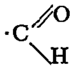
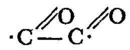
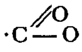
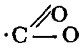
C_{ik} = constant in Equation (1)

C_V = heat capacity at constant volume, cal./mole °K.

c = one-third of number of external degrees of freedom per molecule

d_w = $2\,r_w$, cm.

Table 2c. Standard Energy of Vaporization Increments for Functional Groups Containing Oxygen

Type	Fragment	$E^\circ(\cdot X)$ kcal./mole
Ether		
aliphatic (R_2)*	·O·	$1.60 + \frac{0.40}{N_c}$
hetero-aliphatic (six membered rings)	·O·	1.75
aromatic (φ_2)	·O·	1.0
heteroaromatic†	·O·	1.50
Aldehydes		
aliphatic (R)*		5.20
aromatic (φ)		5.00
Ketones		
aliphatic (R_2)*	:C = O	$2.40 + \frac{3.80}{N_c}$ iso = $n - 0.15\,b$
		
aromatic	:C = O	5.1
Esters		
aliphatic (R_2)		$3.43 + \frac{0.20}{N_c}$
aromatic (φ_2)		3.30

* Normal alkyls.
† Based on only one compound.

E° = standard energy of vaporization = $\Delta H_V - RT$ in cal./mole at T when $V/V_w = 1.70$

$E^\circ(\,)$ = energy of vaporization increment per group in parentheses

f = constant in Equation (5)

Table 2d. Standard Energy of Vaporization Increments for Functional Groups Containing Sulfur

Type	Fragment	$E^\circ(X)$ kcal./mole
Sulfhydryl (Thiol)		
aliphatic (n-alkyl)	·SH	$3.36 + \frac{0.95}{N_c}$
sec-alkyl	·SH	n-alkyl − 0.15
t-alkyl	·SH	n-alkyl − 1.1
aromatic	·SH	3.50
Thioether		
aliphatic (n-alkyl)$_2$	·S·	$2.50 + \frac{2.00}{N_c}$
(*sec*-alkyl)$_2$	·S·	n-alkyl − 0.1/*sec*
cyclic (thiocycloalkane)	·S·	$2.50 + \frac{2.00}{N_c}$
heteroaromatic (thiophene)	— S =	2.90
Disulfides		
aliphatic (n-alkyl)$_2$	·S — S·	$4.40 + \frac{1.90}{N_c}$

TABLE 3. EQUATIONS TO ESTIMATE THE CONSTANT c[*]

(1)	*n*-paraffins:	$3c = 6 + 0.43\,(N_s{}^{**} - 1)/\left(1 + \frac{5.0}{N_s - 1}\right)$
	isoparaffins:	the effect of widely spaced methyl groups is usually negligible. Enough data are generally available to calculate c for highly branched compounds when the need arises.
(2)	*n*-alkyl cyclohexanes:	$3c = 6 + 0.44\,(N_c{}^{\dagger} - 6)$
(3)	*n*-alkyl benzenes:	$3c = 6 + 0.43\,(N_s - 1)/\left(1 + \frac{2.5}{N_s - 1}\right)$
(4)	*n*-alkyl cyanides:	$3c = 6 + 0.43\,(N_s - 1)/\left(1 + \frac{5.3}{N_s - 1}\right)$
(5)	α, ω *n*-alkyl dicyanides:	$3c = 6 + 0.45\,(N_s - 5)$
(6)	aryl mono cyanides:	$3c = 6.6 + 0.4\,(N_s - 1)$
(7)	mono nitro paraffins:	$3c = 6 + 0.43\,(N_s - 1)/\left(1 + \frac{5}{N_s - 1}\right)$
(8)	mono nitro benzenes:	$3c = 6 + 0.4\,(N_s - 1)$
(9)	*n*-alkyl mono nitrates:	$3c = 6 + 0.43\,(N_s - 1)/\left(1 + \frac{5.3}{N_s - 1}\right)$
(10)	alkyl polynitrates:	$3c = 6 + 0.4\,(N_s - 1)/\left(1 + \frac{5}{N_s - 1}\right)$
(11)	(straight chain) aliphatic ethers and acetals, etc:	$3c \approx 5.8 + 0.42\,(N_s - 3)$
(12)	heterocycloaliphatic ethers:	$3c = 6.0 + 0.4\,(N_s - 3)$ for *n*-alkyl ethylene oxides $3c = 4.8 + 0.4\,(N_s - 5)$ for *n*-alkyl tetrahydro furans $3c = 4.2 + 0.4\,(N_s - 6)$ for *n*-alkyl dioxanes
(13)	aliphatic mono carboxylate esters[††] (for $N_c > 10$):	same as *n*-paraffins
(14)	aliphatic α, ω dicarboxylate esters:	$3c = 6.0 + 0.47\,(N_s - 5)$

[*] The equations are given in terms of $3c$, because that is approximately the number of external degrees of freedom (including those due to internal rotation) per molecule, excited in the liquid state in the temperature range corresponding to $V^* = 1.7$ to 1.9.

[†] N_c = total number of carbon atoms per molecule.

[**] N_s = total number of skeletal units per molecule; here the ether oxygen, the carbonyl group, and the NO_2 group are counted as units equivalent to the methyl or methylene groups.

[††] The ρ^* vs. T^* curves of the lower carboxylates do not quite coincide with the master curve of reference *8*.

ΔH_V = heat of vaporization (cal./mole)
J = 4.186×10^7 ergs./cal.
k = Boltzmann constant = 1.38×10^{-16} ergs./°K.
M = molecular weight (g./mole)
m = molecule weight (g./molecule)
N_A = Avogadro number
N_S = number of skeletal atoms per molecule
n = number of external atoms per molecule
R = gas constant = 1.986 cal./mole °K.
r_o = intermolecular distance at equilibrium separation, cm.
r_w = Van der Waals radius, cm.
T = temperature, °K.
T^* = reduced temperature = T/θ_L
V = molal volume cc./mole
V_w = Van der Waals volume, cc./mole (*5*, *6*)
w = weight fraction
X = mole fraction

Greek Letters

ϵ = pair potential (ergs./molecule)
θ_L = reducing parameter for temperature = $E^\circ/5cR$, °K.
λ = thermal conductivity, cal./cm. sec. °K.
λ' = reducing parameter for thermal conductivity = $\frac{R}{N_A\, d_w{}^2}\left(\frac{JE^\circ}{M}\right)^{1/2}$
λ^* = reduced thermal conductivity = λ/λ'
$\lambda_s{}^*$ = defined by Equation (3)
$\lambda_F{}^*$ = defined by Equation (6)
ρ^* = reduced density V_w/V
Ψ = probability that energy is transferred in a collision

LITERATURE CITED

1. Altenburg, K., *Kolloid-Z.*, **117**, 153 (1950).
2. Bekkedahl, N., *Rubber Chem. and Technol.*, 8 (1953).
3. Bondi, A. A., *J. Chem. Phys.*, **19**, 128 (1951).
4. ———, *J. Phys. Chem.*, **58**, 929 (1954).
5. ———, and D. J. Simkin, A.I.Ch.E. Journal, **6**, No. 2, p. 191 (1960).
6. *Ibid.*
7. Brigg, D. K. H., *Ind. Eng. Chem.*, **49**, 418 (1957).
8. Cecil, O. B., and R. H. Mund, *ibid.*, **48**, 437 (1956).
9. Cecil, O. B., et al., *Chem. Eng. Data Ser.*, **2**, 54 (1957).
10. Challone, A. R., and R. W. Powell, *Proc. Roy. Soc.*, **A238**, 80 (1956).
11. Collins, F. C., and H. Raffel, *J. Chem. Phys.*, **29**, 699 (1958).
12. Downie-Smith, J. F., *Trans, Am. Soc. Mech. Engrs.*, **58**, 719 (1936).
13. Ferry, J. D., and G. S. Park, *J. Chem. Phys.*, **4**, 70 (1936).
14. Frontasev, V. P., and M. Y. Gusakov, *Soviet Phys.—Tech. Phys.*, **4**, 1171 (1960).
15. Gollis, M. H., et al., *Preprint C-19*, Div. Petrol. Chem. ACS meeting, New York, New York (September, 1960).
16. Heasell, E. L., and J. Lamb, *Proc. Roy. Soc.*, **A237**, 233 (1956).
17. Helfand, E. L., and S. A. Rice, *J. Chem. Phys.*, **32**, 1642 (1960).
18. Holzmüller, W., and M. Münx, *Kolloid-Z.*, **159**, 25 (1958).
19. Horrocks, J. K., and E. McLaughlin, *Trans. Faraday Soc.*, **56**, 206 (1960).
20. Hudson, G. H., et al., *ibid.*, **56**, 1144 (1960).
21. Kaye, L., *Proc. Roy. Soc.*, **A117**, 459 (1928).
22. Kincaid, F., and H. Eyring, *J. Chem. Phys.*, **6**, 620 (1938).
23. Leng, D. E., and E. W. Commings, *Ind. Eng. Chem.*, **49**, 2042 (1957).
24. Lonsdale, K., *Z. Krist*, **112**, 188 (1959).
25. Nederbragt, G. W., and J. W. M. Boelhouwer, *Brit. J. Appl. Phys.*, Suppl. No. 1, p. 6 (1951).
26. Nernst, W., *Festschr., Ludwig Boltzmann* **1904**, 904 (1904).
27. Owens, E. J., and George Thodos, *A.I.Ch.E. Journal*, **3**, 454 (1957).
28. Phillippov, P., *Proc. Moscow Univ.*, **10**, No. 8, p. 17 (1955).
29. Prigogine, I., "Molecular Theory of Solutions," North-Holland Publishing Company, Amsterdam, Netherlands (1957).
30. Rehner, J., *J. Polymer Sci.*, **2**, 263 (1947).
31. Reid, R. C., and T. K. Sherwood, "The properties of Gases and Liquids," McGraw-Hill, New York (1958).
32. Rice, S. A., and J. G. Kirkwood, *J. Chem. Phys.*, **31**, 901 (1959).
33. Riedel, L., Mitt. kältetechn. Insts. U. Reichsforsch.-Anstalt Lebensmittelfrischhalt. tech. Hochschule Karlsruhe, No. 2 (1948).
34. ———, *Chem. Ing. Tech.*, **13**, 321 (1951).
35. Sakiadis, B. C., and Jesse Coates, *A.I.Ch.E. Journal*, **1**, 275 (1955).
36. *Ibid.*, **3**, 121 (1957).
37. Scheffy, W. J., and E. F. Johnson, *J. Chem. Eng. Data*, **6**, 245 (1961).
38. Vilim, O., *Collection Czechoslov. Chem. Communs.*, **25**, 993 (1960).
39. Zederberg, N. V., and D. L. Timrot, *J. Tech. Phys. (U.S.S.R.)*, **25**, 2458 (1955).
40. Powell, R. W., and A. R. Challoner, *Ind. Eng. Chem.*, **53**, 582 (1961).

Manuscript received September 12, 1961; revision received February 19, 1962; paper accepted February 21, 1962.