μ_{c1} = critical viscosity for methane, micropoise
μ_{c2} = critical viscosity for propane, micropoise
μ_{c01} = atmospheric pressure viscosity at critical temperature for methane, micropoise
μ_{c02} = atmospheric pressure viscosity at critical temperature for propane, micropoise
ρ = density, g./cc.
ρ_m = molar density, g.-mole/cc.
ρ_{cm} = pseudo critical mixture density defined by Equation (2), g./cc.
ρ_r = reduced density, dimensionless
$(\mu_c - \mu_{c0})_m$ = residual mixture viscosity at the pseudo critical point defined by Equation (3), micropoise
$(\mu - \mu_0)_r$ = reduced residual viscosity, dimensionless

LITERATURE CITED

1. Akers, W. W., J. F. Burns, and W. R. Fairchild, *Ind. Eng. Chem.*, 46, 2531 (1954).
2. Bicher, L. B., Jr., and D. L. Katz, *ibid.*, **35**, 754 (1943).
3. Carr, N. L., J. D. Parent, and R. E. Peck, *Chem. Eng. Progr. Symp. Ser. No. 16*, **51**, 91 (1955).
4. Eakin, B. E., and R. T. Ellington, *J. Petrol. Technol.*, **15**, 210 (Feb., 1963).
5. Giddings, J. G., Ph.D. thesis, Rice Univ., Houston, Tex. (1963).
6. Golubev, I. F., and N. A. Agaev, *Dokl. Akad. Nauk SSSR*, **151**, No. 4, 875 (1963).
7. Huang, E. T. S., Ph.D. thesis, Univ. Kansas, Lawrence (1966).
8. ———, G. W. Swift, and Fred Kurata, *AIChE J.*, **12**, 932 (1966).
9. Jossi, J. A., L. I. Stiel, and George Thodos, *ibid.*, **8**, 59 (1962).
10. Lim, B. S., T. S. Huang, J. L. VandenBoom, G. W. Swift, and Fred Kurata, paper presented at 29th Ann. Chem. Eng. Symp. Thermodynamic and Transport Properties on Fluids, Am. Chem. Soc., Rice Univ., Houston, Tex. (Dec., 1962).
11. McCreary, J. G., and G. W. Swift, *Rev. Sci. Instr.*, **35**, 1366 (1964).
12. Prausnitz, J. M., and R. D. Gunn, *AIChE J.*, **4**, 430 (1958).
13. Price, A. R., and Riki Kobayashi, *J. Chem. Eng. Data*, **4**, 40 (1959).
14. Reamer, H. H., B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **42**, 534 (1950).
15. Rossini, F. D., et al., "Selected Values of the Properties of Hydrocarbons and Related Compounds," Carnegie Inst. Technol., Pittsburgh, Pa. (1958).
16. Sage, B. H., and W. N. Lacey, "Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen," Am. Petrol. Inst., New York (1950).
17. Starling, K. E., B. E. Eakin, J. P. Dolan, and R. T. Ellington, "Progress in International Research on Thermodynamics and Transport Properties," p. 530, Academic Press, New York (1962).
18. Starling, K. E., B. E. Eakin, and R. T. Ellington, *AIChE J.*, **6**, 438 (1960).
19. Uyehara, O. A., and K. M. Watson, *Natl. Petrol. News*, Tech. Sect. 36, 764 (Oct. 4, 1944).

Manuscript received July 20, 1966; revision received December 19, 1966; paper accepted December 20, 1966.

On Thermal Conductivity of Liquids

D. S. VISWANATH

Indian Institute of Science, Bangalore, India

The Bridgman equation for thermal conductivity of liquids is examined and a relation between sonic velocity and latent heat of vaporization is given. A correlation based on the hole theory of liquids is presented. This correlation predicts thermal conductivity in the temperature range of —20° to +80°C. for sixteen liquids, and at 20°C. for fifty liquids with an average absolute deviation of 9.5 and 5%, respectively. The correlation is also applied to liquid metals.

A recent paper (*1*) has reviewed the different methods of predicting thermal conductivity K of liquids and shows that the percentage deviation in predicting K values to be about 11% with the proposed method (*1*) used, which is about the same error obtained with the method of Sakiadis and Coates (*1*).

The Bridgman equation for thermal conductivity

$$K = \rho\, c_p U_l L \tag{1}$$

modified as

$$K = 2.8 (N/V)^{2/3} k U_l \gamma^{-1/2} \tag{2}$$

is believed to predict K values with an error of 10% (*2*). Equation (2) has not been tested adequately to assess its usefulness. Another drawback is the requirement of $U_l = f(T)$, if K is to be predicted as a function of temperature.

It is shown here that the velocity of sound in liquids bears a distinct relationship to latent heats of vaporization to predict K values with Equation (2). Furthermore, it is recommended that the constant 2.8 in Equation (2) be changed to 2.4 for better agreement with experimental values.

RELATION BETWEEN VELOCITY OF SOUND AND LATENT HEAT OF VAPORIZATION

Eyring and co-workers (*3*), who are mainly responsible for developing the concept of molecular holes in liquids, represent the partition function of a molecule in the liquid by the expression

$$F_l = \frac{(2\pi\, mkT)^{3/2}}{h^3} v_f b_l e^{-E_0/RT} \tag{3}$$

where E_0 is taken to be the difference in energy, per mole, between the molecules in the liquid and in the gas at 0°K. It is assumed in the present work that E_0 can be replaced by E, and therefore it is approximately equal to ΔH. This of course reduces to ΔE at 0°K. With this, the Eyring equation for the ratio of free volume to the volume inhabited by a molecule becomes

$$\frac{V_f^{1/3}}{V^{1/3}} = \frac{CRT}{\Delta H} = \frac{U_g}{U_l} \tag{4}$$

Table 1. Relation Between Velocity of Sound and Latent Heat of Vaporization

Substance	Temp., °K.	273	283	293	303	313	323	Max. % dev. from av. value
Pyridine	(1)	598	581	564	548	531	516	—
	(2)	1.195	1.203	1.205	1.220	1.230	1.240	2.00
	(3)	0.950	0.950	0.950	0.950	0.955	0.955	0.3
Diethyl ether	(1)	405	390	375	360	346	332	—
	(2)	0.860	0.855	0.843	0.825	—	—	2.5
	(3)	0.643	0.639	0.631	0.627	0.622	0.614	2.5
Heptane	(1)	554	536	518	499	485	469	—
	(2)	0.968	0.968	0.968	0.968	0.966	0.966	0.0
	(3)	0.880	0.880	0.874	0.874	0.872	0.867	0.7

(1) = $(\Delta H/T^{1/2})$; (2) = $U_l/(U_l)_{\text{octane}}$; (3) = $\Delta H/(\Delta H)_{\text{octane}}$.

Using the kinetic theory relation $U_g = (RT\gamma/M)^{1/2}$, one obtains

$$U_l = (\gamma/MC^2R)^{1/2}\,(\Delta H/T^{1/2}) \tag{5}$$

Equation (5) shows a linear relation between U_l and $(\Delta H/T^{1/2})$ if γ is assumed to be a constant. The linear relation between U_l and $\Delta H/T^{1/2}$ can be established also from different arguments as shown below.

The Lewis (*4*) equation for the velocity of sound in a liquid is

$$U_l^2 = \frac{\Delta H \gamma}{\alpha T} \tag{6}$$

where α is the coefficient of thermal expansion. Using the thermodynamic relation

$$\gamma = 1 + (T\,\alpha^2 U_l^2/c_p) \tag{7}$$

we get from Equation (6)

$$U_l^2 = \frac{\Delta H}{\alpha\,T\,\{1 - \alpha\,\Delta H/c_p\}} \tag{8}$$

Equation (8), on expansion, yields

$$U_l^2 = (\Delta H^2/c_pT) + (\Delta H/T)(1/\alpha) \tag{9}$$

By using the definition of α, and approximating $(ds/dp)_T$ by $(\Delta s/\Delta p)_T$, the second term on the right-hand side of Equation (9) becomes $V\,\Delta p$. As $V\,\Delta p$ is small, the term can be neglected. Finally, one gets

$$U_l^2 = \Delta H^2/c_pT \tag{10}$$

The specific heat c_p of the liquid can be taken to be a linear function in temperature. Utilizing this, we can write from Equation (10)

$$U_l = (\Delta H/T^{1/2})\,\{1/(a + bT)^{1/2}\} \tag{11}$$

Expanding Equation (11) in Taylor's series, we get

$$U_l = (\Delta H/T^{1/2})\left\{\frac{1}{a^{1/2} + bT/2a^{1/2}}\right\} \tag{12}$$

As the coefficient $b << a$, Equation (12) establishes the linear relationship between U_l and $\Delta H/T^{1/2}$.

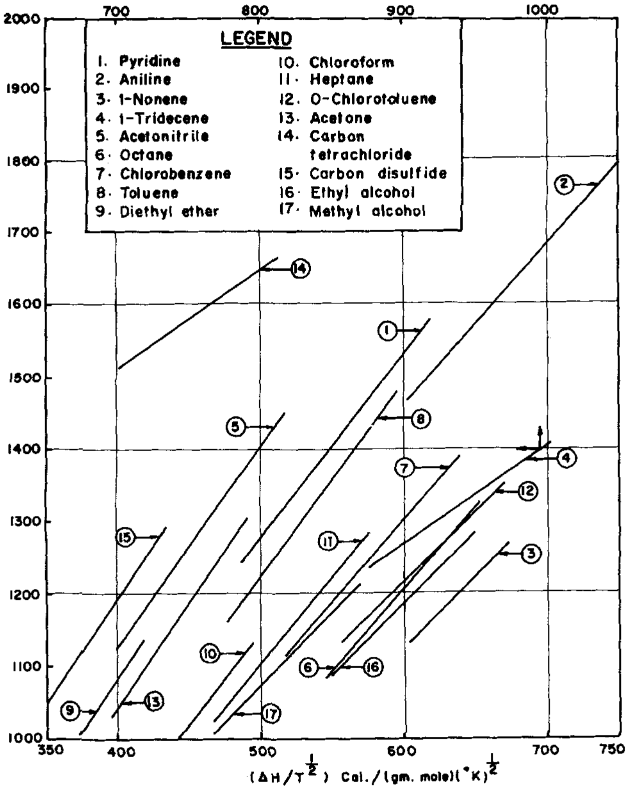

Fig. 1. Velocity of sound as a function of heat of vaporization.

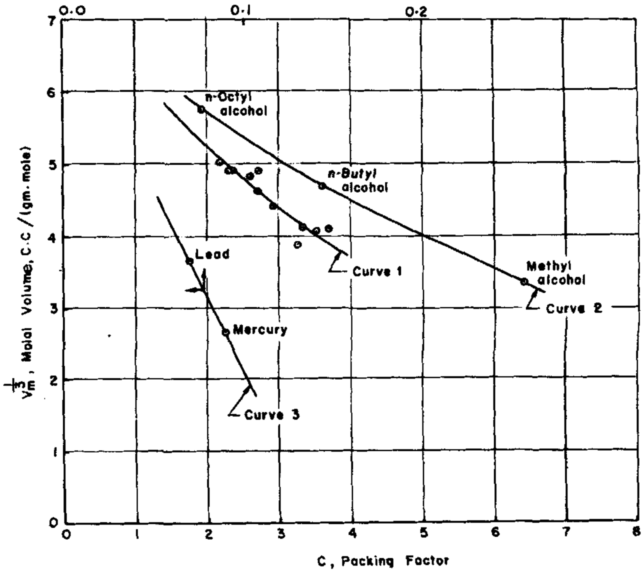

Fig. 2. Packing factor as a function of molal volume.

Figure 1 shows the validity of such a relation. Because of the excellent relationship, U_l can be replaced by $(\Delta H/T^{1/2})$. Thus Equation (2) finally becomes

Table 4. Predicted and Experimental Thermal Conductivity of Alcohols

	K × 10^3 Exptl.	K × 10^3 Calcd.	% Error	% Error*
Methyl alcohol	0.483	0.483	0.00	− 6.85
Ethyl alcohol	0.421	0.410	−2.60	+ 2.70
Allyl alcohol	0.429(30°C.)	0.407	−5.10	+11.00
n-Propyl alcohol	0.395	0.390	−1.30	+12.20
n-Butyl alcohol	0.380	0.355	−6.60	+19.40
Isobutyl alcohol	0.342	0.348	+1.75	+40.50
Isoamyl alcohol	0.364(30°C.)	0.345	−5.20	+36.00
n-Heptyl alcohol	0.384	0.386	+0.52	+16.60
n-Octyl alcohol	0.397	0.398	0.0	+34.00
Isopropyl alcohol	0.349	0.370	+6.00	+34.00

* Values taken from reference *1*.

$$K = 2.4(N/V)^{2/3}\,k\,\{A(\Delta H/T^{1/2}) + B\} \qquad (13)$$

Two values of U_l and $\Delta H/T^{1/2}$ are required to evaluate A and B in Equation (13). Choosing a reference substance, we find that the empirical relations

$$U_l/(U_l)_{yef} = \text{constant} \qquad (14a)$$

and

$$\Delta H/(\Delta H)_{yef} = \text{constant} \qquad (14b)$$

hold well when the property is taken at the same temperature. It is therefore possible to find U_l as a function of temperature with one value of U_l and Equation (14*a*). This relation is particularly useful in the range 0° to 50°C. Table 1* shows the validity of Equations (14*a*) and (14*b*). Seventeen substances shown in Figure 1 were tested, and the results tabulated as shown in Table 1. For any particular substance the maximum percentage deviation from the average value of the ratios $U_l/(U_l)_{\text{octane}}$ and $\Delta H/(\Delta H)_{\text{octane}}$ in the range of 0° to 50°C. was found to be 5.6 and 2.5, respectively.

For any two temperatures, and for a particular substance, Equations (5) and (10) reduce to

$$(U_l)_1/(U_l)_2 = (\Delta H_1/\Delta H_2)(T_2/T_1)^{1/2} \qquad (15a)$$

and

$$(U_l)_1/(U_l)_2 = (\Delta H_1/\Delta H_2)(c_{p2}\,T_2/c_{p1}\,T_1) \qquad (15b)$$

respectively. Equations (15*a*) and (15*b*) also permit the evaluation of U_l as a function of temperature from a knowledge of one value of U_l, and ΔH or ΔH and c_p as the function of temperature. Watson's relation for latent heats can be used in Equations (15*a*) and (15*b*), thus eliminating the requirement of a knowledge of ΔH as a function of temperature.

In the evaluation of K values with Equation (13) used, the values of velocity of sound were drawn from the data given by Fryer et al. (*5*), Lagemann et al. (*6*, *7*), and Rao (*8*). The latent heat values were either taken from Perry (*9*) or evaluated by using the 0.38 latent heat law of Watson (*10*). The improvement effected in using Equation (13) was not substantial, although the relation was better at higher temperatures of 30° and 40°C. Detailed tabular material and a comparison of Equation (13) with the method of Pachiyappan et al. (*1*) can be found in Table 2.* The average absolute percentage deviation for ten compounds tested for sixteen points was found to be 9.0. This is comparable to the correlation proposed recently (*1*).

AN IMPROVED CORRELATION

From Equations (2) and (5) we can write

$$K = \frac{3.6 \times 10^{-4}\,\Delta H_b}{C V_m^{2/3} M^{1/2} T^{1/2}} \left(\frac{1 - T_r}{1 - T_{rb}}\right)^{0.38} \qquad (16)$$

Equation (16) is a theoretically sound relation, except for the use of the empirical Watson relation:

$$\Delta H = \Delta H_b \left(\frac{1 - T_r}{1 - T_{rb}}\right)^{0.38} \qquad (17)$$

A previous paper (*10*) gave a semitheoretical justification for the Watson 0.38 latent heat law. The packing factor C is normally assumed as 2. As the other quantities in Equation (16) are known or can be predicted with greater accuracy than K, the error in predicting K is attributed to the packing factor C. Using the experimental K values, we calculated the packing factor. This is done only for ten liquids and it is shown as a function of $V_m^{1/3}$ in Figure 2.

The values of K were then calculated with the value of C from Figure 2. Forty organic compounds, including acids, hydrocarbons, esters, halogenated compounds, etc., were used in testing Equation (16). The maximum and average absolute percentage deviations were found to be 19.0 and 6.2%, respectively. Detailed tabular material and a comparison with the method of Pachaiyappan et al. (*1*) as Table 3 can be found elsewhere.*

In the case of alcohols a separate C vs. $V_m^{1/3}$ curve was obtained with experimental K values of three alcohols. The K values for the rest of the alcohols were predicted and the results are shown as Table 4. In both Tables 3 and 4 the ΔH values used were those corrected with the Watson 0.38 latent heat law and ΔH_b; where adequate data were not available to convert the ΔH_b value to the value at the desired temperature, the ΔH value used was ΔH_b multiplied by 1.1. From the known values of ΔH for several substances in the range of 20° to 40°C., and ΔH_b the relation

$$\Delta H = 1.1\,\Delta H_b \qquad (18)$$

was found to be satisfactory. Experimental K values are drawn from reference *1*.

The correlation was tried in the case of liquid metals with fair results. The C vs. $V_m^{1/3}$ curve was established with the experimental K values of lead and mercury. Table 5 shows the results. It is likely that a ± 20% accuracy can be expected. In the case of sodium and potassium, as V_m values were not available, the density given by Kleppa (*13*) has been used. In the case of tin, the value given is for temperature in the range of 232° to 332°C. Therefore, an average temperature is used. It can

Table 5. Thermal Conductivity of Liquid Metals

Substance	Temp., °C.	$K_{\text{Exptl.}}$	$K_{\text{Calcd.}}$	% Error	Data Source
Lead*	700	0.036	0.036	0.0	*11*
Lead	500	0.037	0.0404	9.2	*11*
Mercury*	120	0.0261	0.0261	0.0	*11*
Sodium†	100	0.2055	0.180	12.4	*11*
Bismuth	273	0.037	0.044	19.0	*12*
Tin	280	0.078	0.098	20.0	*12*

* Values used to establish curve 3 in Figure 2.
† Latent heat values corrected to 100°C.

---

* The values presented herein are typical of results. A tabulation for all the seventeen substances has been deposited as document 9441 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D.C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

TABLE 6. THERMAL CONDUCTIVITY AS A FUNCTION OF TEMPERATURE

Substance	Temp., °C.	Packing factor, C	ΔH, cal./g. mole	$K_{\text{Exptl.}} \times 10^6$	$K_{\text{calcd.}} \times 10^6$	% Dev.
Carbon tetrachloride	−20	2.6	8,270	275	271	− 1.4
	20		7,860	247	240	− 2.8
	40		7,610	237	223	− 5.5
	50		7,500	234	217	− 7.3
	65		7,300	231	207	−10.4
Ethyl alcohol	20	5.2	10,500	421	410	− 2.6
	30		10,340	412	397	− 3.6
	40		10,200	403	387	− 4.0
	60		9,780	386	356	− 7.7
Chlorobenzene	−20	2.4	10,580	328	400	+22.0
	20		10,100	308	356	+15.8
	40		9,950	298	338	+13.4
	60		9,700	290	319	+10.0
n-Hexane	20	2.02	7,620	314	313	− 0.5
	30		7,550	304	307	+ 1.0
	60		7,100	272	275	+ 1.0

% Dev. = (calcd. − exptl.)/exptl. × 100.

be concluded from Figure 2 and Tables 4 and 5 that separate C vs. $V_m^{1/3}$ relations for homologous series improve very much the accuracy in predicting thermal conductivity values.

TEMPERATURE DEPENDENCE

The improved correlation Equation (16) shows that thermal conductivity of liquids is directly proportional to latent heat of vaporization and inversely proportional to the square root of the absolute temperature. All the sixteen organic substances considered by Reid and Sherwood (*14*) were used to test Equation (16). Table 6 shows the results of such a test. Detailed tabular material for the sixteen substances deposited as Table 6 can be found elsewhere.*

Methyl alcohol was one of the substances used to establish the C vs. $V_m^{1/3}$ curve for alcohols. The value of K used was 483×10^{-6} (*1*) at 20°C. The values quoted by Reid and Sherwood (*14*) at 40° and 60°C. are 487 and 421×10^{-6}, respectively. So the errors in prediction might be also because of the unreliable conductivity values. But the usefulness of Equation (16) to predict K values at different temperatures is well substantiated by Table 6. Fifty points were considered and the overall average absolute percent deviation was found 9.5. Five (chloro-, bromo-, iodobenzenes, methylene chloride, and oxylene) out of the sixteen substances considered gave rather large deviations, ranging between 10 to 32%. Except for these five compounds, the average absolute percent deviation will be 5%. This further shows that separate C vs. $V_m^{1/3}$ curves for different homologous series should be established for accurate prediction of thermal conductivity values. In the case of n-butyl alcohol a ΔH value of 11,500 was used, as necessary data to use Watson's relation were not available. All the latent heat values listed in Table 6 were calculated with Watson's relation.

A more realistic approach may be to use both C and V values at the particular temperature instead of using molal volumes at the normal boiling point calculated with the Le Bas method. The V_m values used in this work were those given by Pachaiyappan et al. (*1*). The question of temperature dependence of ΔH and V has been omitted by the authors (*1*). Furthermore, each property can be treated as a function of temperature, thus establishing K as a function of temperature only.

NOTATION

a, b = constants in specific heat relation
A, B = constants in velocity of sound in liquid relation
b_l = vibrational and rotation contribution to partition function
C = packing factor
c_p = specific heat at constant pressure, cal./(g.)(°C.)
E_o = internal energy of vaporization at 0°K.
E = internal energy of vaporization at T°K.
F_l = partition function of a molecule in the liquid
h = Planck's constant
k = Boltzmann constant
K = thermal conductivity, cal./(cm.)(sec.)(°C.)
L = intermolecular clearance, cm.
m = mass of a molecule
M = molecular weight
N = Avogadro's number
R = gas constant
T = temperature, °K.
T_r = reduced temperature, T/T_c
U_g = velocity of sound in the gas, meter/sec.
U_l = velocity of sound in the liquid, meter/sec.
V = molal volume at temperature, T°K.
V_f = molecular free volume
V_m = molal volume at normal boiling point

Greek Letters

α = coefficient of thermal expansion
γ = ratio of specific heats
ΔH = latent heat of vaporization at temperature T°K.
ρ = density, g./cc.

Subscript

b = property at the normal boiling point

LITERATURE CITED

1. Pachaiyappan, V., S. H. Ibrahim, and N. R. Kuloor, *J. Chem. Eng. Data*, **11**, 73 (1966).
2. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," p. 634, Wiley, New York (1954).
3. Glasstone, S., K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," Chap. IX, McGraw-Hill, New York (1941).
4. McG Lewis, W. C., *Z. Phys. Chem.*, **78**, 24 (1912).
5. Fryer E. B., J. C. Hubbard, and D. H. Andrew, *J. Am. Chem. Soc.*, **51**, 759 (1929).
6. Lagemann, R. T., D. R. McMillan, Jr., and W. E. Woolf, *J. Chem. Phys.*, **17**, 369 (1949).
7. Lagemann, R. T., et al., *ibid.*, **16**, 247 (1948).
8. Rao, M. R., *Indian J. Phys.*, **14**, 109 (1940).
9. Perry, J. H., ed., "Chemical Engineers' Handbook," 4 ed., McGraw-Hill, New York (1954).
10. Viswanath, D. S., and N. R. Kuloor, *J. Chem. Eng. Data*, **11**, 69 (1966).
11. Bird, R. B., W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena," p. 248, Wiley, New York (1960).
12. Kirk, R. E., and D. F. Othmer, "Encyclopedia of Chemical Technology," Vol. 2, 14, Interscience, New York (1948, 1955).
13. Kleppa, O. J., *J. Chem. Phys.*, **17**, 668 (1949).
14. Reid, R. C., and T. K. Sherwood, "Properties of Gases and Liquids," pp. 254-256, McGraw-Hill, New York (1956).

Manuscript received July 13, 1966; revision received December 20, 1966; paper accepted December 21, 1966.

---

* See footnote on page 852.