Studies of Thermal Conductivity of Liquids

BYRON C. SAKIADIS and JESSE COATES

Louisiana State University, Baton Rouge, Louisiana

Part III

Values of thermal conductivity and temperature coefficients for thirty-five pure organic liquids, in addition to those previously reported, obtained with a previously described apparatus (Part I), are presented. Values of thermal conductivity or temperature coefficients for twenty-eight of these liquids have not been reported before. The experimentally determined maximum error is ±1.0%.

The two methods for predicting the thermal conductivity of liquids previously proposed (Parts I and II) are extended to cover the types of compounds studied in this investigation, in particular ring compounds.

The temperature coefficient of thermal conductivity was observed to decrease rapidly, approaching zero as the freezing point is approached. The existence of a transition temperature or region within the liquid state is shown and identified with the onset of molecular rotation.

This part of the series presents the results of a continuing study of the thermal conductivity of liquids and associated phenomena. The experimental apparatus was described in Part I, where the results of tests on fifty-three pure organic liquids, chain-type compounds, were reported. In this part the study was extended to new types of compounds, in particular to cyclic compounds, aromatics, and naphthenes, with side chains.

The data were correlated with the two methods previously proposed in Parts I and II. These methods represent different approaches to the problem. The method involving the theoretical equation throws light on the effect of molecular structure on thermal conductivity. The method involving a correlation of thermal conductivity as a function of reduced temperature emphasizes the effect of the functional atom or group in the molecule.

It was considered important also to investigate the variation of thermal conductivity with temperature in the regions close to the boiling and freezing points. The results are direct evidence of a new kind in support of the relatively recent idea on the existence of a transition temperature in the liquid state.

Experimental

The thermoconductimetric apparatus used in this study was described in detail in earlier publications (*9, 10*), where the results of a number of tests were also presented. The experimental procedure and method of calculation remain unchanged.

Results

The results obtained from the experimental determinations are presented in Table 1. The purity and sources of the chemicals are also indicated. The thermal conductivity of most liquids was determined at three temperatures equally spaced over the indicated temperature range, and the temperature coefficient was calculated from the results.

The experimentally determined maximum error in the value of thermal conductivity of liquids is ±1.0%.

Comparison with Literature Values

An extensive literature survey has been made (*7, 8*), and values of thermal conductivity for numerous liquids have been collected, classified, and evaluated. Excluding the results of Bridgman, Daniloff, and Smith (*7*), determined with the same thin-film apparatus, which are high, the more dependable results fall mainly in two groups differing consistently by about 5%. The first group comprises the results of Riedel and Mason (*7, 8*) determined with similar but not identical thin-film apparatus. The second group comprises the results of Bates and Slawecki (*7, 8*), determined with thick- and thin-film apparatus respectively. The reported results differ in two respects. The values of thermal conductivity of the first group are low by about 5%, and the values of the temperature coefficient of thermal conductivity are also low. The results of the authors determined with a variable-film-thickness apparatus agree with the results of the second group.

It was shown by the authors (*9, 10*) that the consistent difference in the values of thermal conductivity of the two groups is due to surface effects and irregularities which were not accounted for by Riedel and Mason in the measurements of the liquid-film thickness by direct measurements.

In the apparatus used by Bates the liquid layer was about 2 in. thick, and the liquid-film thickness was measured directly within the liquid layer. Hence the results should be free of any surface effects. Slawecki used a concentric type of thin-film apparatus but measured the liquid-layer thickness with electrical capacitance methods, thus obtaining a more representative average thickness. In the apparatus used by the authors the liquid-layer thickness is variable, and by means of a special method of calculation (*10*) the effect of surface films and irregularities is eliminated.

A comparison of reported values of the temperature coefficient of thermal conductivity with the authors' results shows that in all concentric types of thin-film apparatus, including that used by Slawecki, consistently low values are obtained. These are probably due to the expansion of the copper cylinders, at the higher operating temperatures, in the concentric type of apparatus used by these investigators. The results of Bates are consistently higher, but the effect has been traced (*10*) to the effects of heat transfer by radiation across the liquid layer, which were neglected by Bates.

DISCUSSION OF RESULTS

The thermal conductivity of liquids has been observed to vary linearly with temperature. In condensing apparatus the thermal conductivity of the liquid film at the boiling point is usually estimated by extrapolation of low-temperature data. It is important that this procedure be verified experimentally. Accordingly, the thermal conductivity of cyclopentane, cyclohexane, and ethyl alcohol was determined at temperatures close to the boiling point:

Liquid	Highest observed temperature, °F.	Boiling point, °F., at 1 atm.
Ethyl alcohol	167.0	173.1
Cyclopentane	116.7	120.7
Cyclohexane	168.7	177.4

Parts I and II appeared in the *A.I.Ch.E. Journal*, vol. 1, No. 3, p. 275 (1955).

B. C. Sakiadis is with E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware.

The results show that the thermal conductivity varies linearly with temperature near the boiling point.

The region close to the freezing point is equally important. The thermal conductivity of *n*-dodecane, *n*-tetradecane, *n*-hexadecane, and *n*-octadecane was therefore determined at temperatures close to the freezing point. (*n*-Octadecane is a solid at room temperature.) The results are shown in Figure 1. The scatter of the data is within the maximum experimental error of ±1.0%. The results show that the thermal conductivity is not a linear function of temperature as the freezing point is approached. Although *n*-dodecane does not show such behavior, it is clear that at sufficiently low temperatures, outside the range of this apparatus, it could be expected to behave similarly.

The plots of Figure 1 bring up a number of interesting points. As the freezing point is approached, the temperature coefficient of thermal conductivity decreases rapidly toward zero. The thermal conductivity is observed to vary little with temperature in the region above the freezing point (14.7, 41.9, 64.6 and 81.9°F. for C_{12}, C_{14}, C_{16}, and C_{18} respectively).

Another point of interest is the shape of the curves in Figure 1. The curves show that there is a region where the thermal conductivity drops sharply—about 4%—with a small temperature increase. In view of the fact that the temperature drop across the liquid layer in this apparatus is about 10°F., it is not certain whether this rapid drop extends over a range or whether it indicates transition phases with a sudden discontinuity. The idea of transition phases within the solid state is not new. A number of solid paraffins (*3, 5, 13*), alcohols (*1*), esters (*2*), and bromides (*4*) exhibit discontinuous changes in a number of physical properties at a transition temperature which have been attributed to the onset of hindered molecular rotation. The idea of transition phases within the liquid state is more recent. Moore, Gibbs and Eyring (*6*) conclude that far from being an amorphous and random aggregation of molecules, liquids not only possess a substantial degree of order, but many exhibit several recognizable transitions in addition to the solid-to-liquid and liquid-to-gas transitions. By considering the molecules in the liquid state to be arranged in a way similar to that adopted by the authors for the prediction of thermal conductivity (*11*), they suggest that many physical properties, when plotted against temperature, show abrupt discontinuities or transition temperatures. To confirm these ideas the authors have plotted properties for a large number of liquids as suggested by Moore, Gibbs, and Eyring. Careful consideration of the results leads to the conclusion that although there is some evidence for transition temperatures, it is far from being conclusive and the transition temperatures are difficult to establish. The authors believe that any transition temperatures present in the liquid state should be related to the transition temperatures observed in the solid state. Plots of freezing and transition points as functions of temperature for the solid paraffins (*3, 5*) show that transition temperatures appear only for the C_{25} to C_{38} paraffins. For paraffins with fewer than twenty-five carbon atoms the transition-temperature curve crosses the freezing-point curve. Transition temperatures in the solid state have been observed also for the first three members of the paraffin series. It is possible then that for the C_3 to C_{25} paraffins the transition temperature exists in the liquid state. The evidence on thermal conductivity presented by the authors appears to substantiate this idea. The observed transition region may then be identified with the onset of molecular rotation above which the molecules can rotate about their long axis or are "rotationally active." Qualitatively this may be visualized as follows. At a given temperature above the freezing point the molecules have a certain capacity to absorb energy for transfer. At the transition temperature part of this energy must be

TABLE 1.

OBSERVED VALUES OF THERMAL CONDUCTIVITY

Liquid	k at 100°F., B.t.u./(hr./sq. ft.)(°F./ft.)	$dk/dt \times 10^{-}\times$, B.t.u./(hr./sq. ft.)(°F./ft.)/°F.	Temperature range, °F.	Source purity
Methyl ethyl ketone	0.0850	−1.68	103–152	4-c
Diethyl ketone	0.0830	−1.40	96–169	4-c
Methyl *n*-propyl ketone	0.0807	−1.40	102–169	4-c
2-Heptanone	0.0785	−1.20	107–169	2-b
3-Heptanone	0.0792	−1.13	110–169	2-e
4-Heptanone	0.0792	−1.22	103–169	2-e
2-Octanone	0.0796	−1.20	92–169	2-e
n-Butyl-ethyl ether	0.0725	−1.30	104–169	2-b
Di-*n*-butyl ether	0.0748	−1.30	101–169	2-b
Di-*n*-hexyl ether	0.0786	−1.12	101–169	2-b
1, 2-Bis (2-methoxy ethoxy) ethane	0.0942	−1.40	91–167	2-b
Ethylene glycol monomethyl ether	0.1064	−1.27	96–170	1-e
Ethylene glycol monoethyl ether	0.0982	−1.30	96–164	1-e
Ethylene glycol monobutyl ether	0.0904	−1.20	95–165	1-e
Diethylene glycol monomethyl ether	0.1048	−0.95	101–165	1-e
Diethylene glycol monoethyl ether	0.1109	−0.88	101–164	1-e
Diethylene glycol monobutyl ether	0.0930	−0.90	101–165	1-e
Cyclopentane	0.0729	−1.09	90–117	5-a
Methyl cyclopentane	0.0666	−1.00	102–138	5-a
Cyclohexane	0.0686	−1.03	97–169	5-a
Methyl cyclohexane	0.0629	−0.97	104–168	5-a
Cyclohexene	0.0747	−1.20	98–165	5-a
Cyclohexanone	0.0817	−1.33	98–169	4-c
i-Propyl benzene	0.0715	−1.35	89–134	5-a
n-Butyl benzene	0.0758	−1.19	89–133	5-a
n-Dodecane	0.0797	−1.17	100–167	4-c
n-Tetradecane*	0.0794	−0.95	110–167	3-d
n-Hexadecane*	0.0819	−0.90	110–167	3-d
n-Octadecane*	0.0844	−0.85	110–167	3-d
Heptene-3	0.0749	−1.25	92–138	3-d
2, 4-Dimethyl pentane	0.0587	−1.00	100–152	5-a
t-Amyl alcohol	0.0682	−0.90	104–169	2-d
Heptanol-3	0.0801	−1.00	92–167	1-e
n-Decyl acetate	0.0818	−1.28	96–168	4-c
1-Bromodecane	0.0669	−0.86	98–169	2-b

---

*The given value of thermal conductivity is at 110°F. This value can be extrapolated to higher temperatures only. For values at lower temperatures *see* Figure 1.

Source

1. Carbide and Carbon Chemicals Co.
2. Eastman Organic Chemicals
3. Humphrey-Wilkinson, Inc.
4. Matheson Coleman and Bell, Inc.
5. Phillips Petroleum Co.

Purity

a. Pure—99 mole % min.
b. "Eastman"—highest purity
c. Research—98% highest feasible purity
d. 95% min.
e. Practical

retained by the molecules to initiate rotation. As a result, the net energy transfer and thermal conductivity decrease sharply.

Two other points should be mentioned. (1) The position of the OH group in the alcohol molecule seems to play an important role: the thermal conductivity of heptanol-3 is much lower than that of *n*-heptyl alcohol. (2) The position of the functional group in a molecule (ether, ketone, or ester) having the same total number of carbon atoms does not affect the thermal conductivity.

The value of thermal conductivity of diethylene glycolmonoethyl ether is much higher than either the monomethyl or monobutyl member. This liquid is specified as low gravity by the supplier, and the effect is probably due to impurities. Literature data (*8*) confirm this observation.

CORRELATIONS OF THERMAL CONDUCTIVITY

Correlations of thermal conductivity are important for process calculations. Two general methods of predicting the thermal conductivity as a function of temperature were proposed by the authors (*10, 11*). In this paper the methods are extended to include the new data.

Correlation Based on a Modified Statement of the Theory of Corresponding States

According to this method the ratio of the thermal conductivity of two members of a given homologous series, at a given reduced temperature, is the same as that of the corresponding two members of any other homologous series at the same reduced temperature. The reduced pressure is omitted from the correlation, as at 1 atm. the effect of differences in reduced pressure on thermal conductivity is small.

The thermal conductivity of different homologous series was correlated as a function of reduced temperature with the number of effective carbon atoms as a parameter. The contribution to the thermal conductivity of a given functional group or atom in the molecule was determined by using the *n*-aliphatic hydrocarbons as a basis and taking the difference between it and the series in question at a reduced temperature $T_r = 0.6$. This temperature was selected in order to reduce the extrapolation of the experimental data. The contributions to the thermal conductivity were determined for ethers, ketones, monoglycol ethers, diglycol ethers, tertiary alcohols, naphthenes, and aromatic hydrocarbons. The results are shown in Table 2. The generalized chart for *n*-aliphatic hydrocarbons is shown in Figure 2. In this chart the line marked 12-18 should be used only if the molecules are "rotationally active," or about 70°F. above the freezing point. The convergence

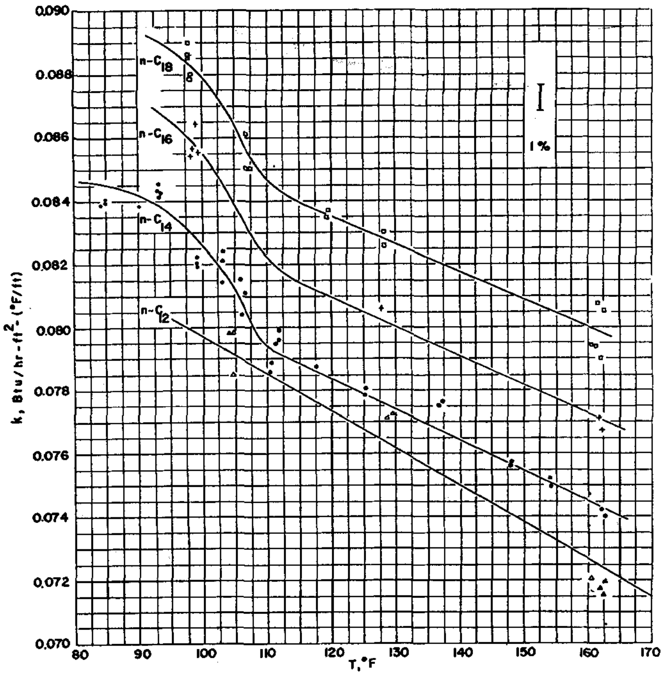


Fig. 1.

TABLE 2

STRUCTURAL CONTRIBUTION TO THE THERMAL CONDUCTIVITY OF LIQUIDS AT $T_r = 0.6$

A. Straight chain, saturated Basis: *n*-Aliphatic hydrocarbons	*dk*, B.t.u./(hr./sq. ft.) (°F./ft.)	Effective number of carbon atoms, *x*
Series		
Hydrocarbons, $C_nH_{2n} + 2$	0	$x = n$
Alcohols, $C_nH_{2n+1}OH$	+0.0070*	$x = n$
Esters, $C_nH_{2n}O_2$	−0.0070	$x = n - 2$
Halides, $C_nH_{2n+1}Cl$	−0.0168	$x = n$
$C_nH_{2n+1}Br$	−0.0248	$x = n + 1$
$C_nH_{2n+1}I$	−0.0310	$x = n + 2$
Nitro, $C_nH_{2n+1}NO_2$	0*	$x = n$
Ethers, $C_nH_{2n+2}O$	−0.0061	$x = n - 2$
Ketones, $C_nH_{2n}O$	−0.0041	$x = n - 2$
Monoglycol ethers, $C_nH_{2n+2}O_2$	0	$x = n - 2$
Diglycol ethers, $C_nH_{2n+2}O_3$	+0.0082	$x = n - 2$

B. Cyclic compounds

I. Aromatic hydrocarbons

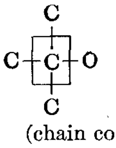
Basis: Benzene† $k = 0.0800$ B.t.u./(hr./sq. ft.)(°F./ft.)

For contribution of added —CH$_2$—, —CH$_3$ groups in straight chain, consider benzene as ethane and determine contribution of groups as for *n*-aliphatic hydrocarbons.

II. Naphthenes

Basis: Cyclopentane. $k = 0.0738$ B.t.u./(hr./sq. ft.)(°F./ft.)

Contribution for each additional —CH$_2$—, or - -CH$_3$ in ring or straight chain = −0.0083 B.t.u./(hr./sq. ft.)(°F./ft.)

C. Isomerization Type	*dk*, B.t.u./(hr./sq. ft.)(°F./ft.)
For one —CH$_3$ group	−0.0060
For two —CH$_3$ groups	−0.0104
For three —CH$_3$ groups	−0.0142
Tert-alcohols  $C-\overset{C}{\underset{C}{C}}-O$	−0.0155
D. Bonding (chain compounds)	
One double bond =	+0.0010

---

*The first members of the high-polarity series, such as alcohols and nitrated alkanes, have a specific line as shown in Figure 2.

†This value for benzene has been obtained by extrapolation from the higher members.

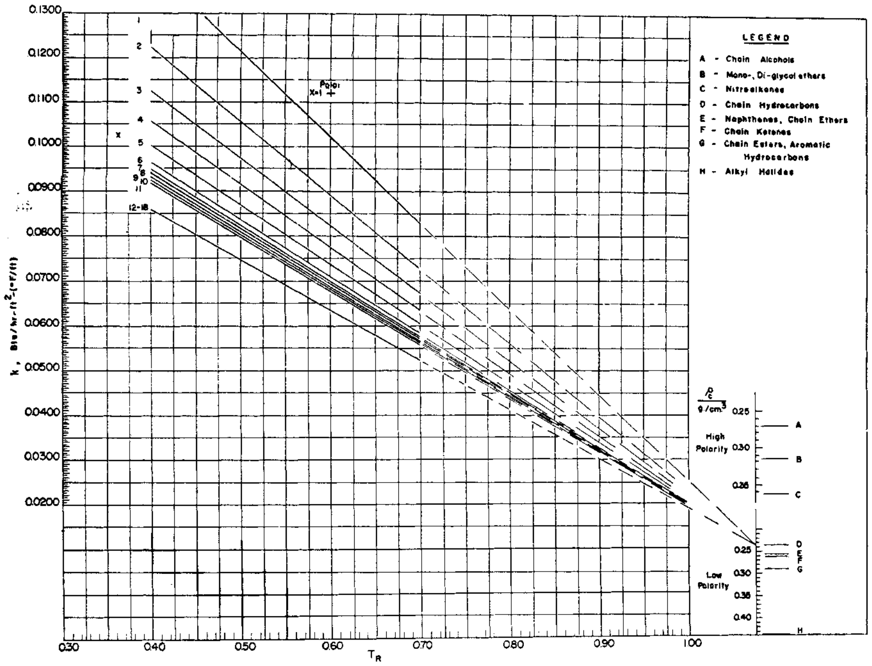


Fig. 2. Thermal conductivity vs. reduced temperature.

points of the different series are marked by letters but can be located also from the critical density of the series. Although the critical density varies somewhat from member to member, an average value for two or three members is sufficient to locate the point. In this way the thermal conductivity for an entire series of liquids, at any temperature, can be estimated from a single known value. This value can be estimated by the previously presented (*11*) theoretical method.

TABLE 3

A. Reference Points for Thermal Conductivity

Effective No. of carbon atoms, x	k, B.t.u./(hr./sq. ft.) (°F./ft.) at $T_r = 0.6$
1*	0.1022
2	0.0894
3	0.0822
4	0.0776
5	0.0738
6	0.0709
7	0.0700
8	0.0693
9	0.0687
10	0.0681
11	0.0675
12–18	0.0635

B. Coordinates for Critical-density Scales

1. Low-polarity series

ρ_c, g./cc.	k, B.t.u./(hr./sq. ft.) (°F./ft.) at $T_r = 1.075$
0.20	0.0145
0.25	0.0095
0.30	0.0045
0.35	−0.0005
0.40	−0.0055
0.45	−0.0105

2. High-polarity Series

ρ_c, g./cc.	k, B.t.u./(hr./sq. ft.) (°F./ft.) at $T_r = 1.075$
0.25	0.0411
0.30	0.0328
0.35	0.0245

The only data required in drawing Figure 2 are the reference values of k at $T_r = 0.6$ for the hydrocarbon series and the coordinates of the critical-density scales. These data are given in Table 3.

This method of calculation will be illustrated by two examples.

ILLUSTRATION 1. Calculate the thermal conductivity of *i*-propyl benzene at 120°F.

Data: T_c = 1,145°R.	k
Basis: Benzene at $T_r = 0.6$	0.0800
For contribution of *i*-propyl group, consider benzene as ethane; take the difference in k between ethane and *n*-pentane (or three carbon groups) at $T_r = 0.6$ from chart. The difference is subtracted since the thermal conductivity decreases with increasing molecular size.	
−[0.0894 (ethane) − 0.0738 (*n*-pentane)] =	−0.0156
1 isomerization	−0.0060
	0.0584

In Figure 2 locate this point at $T_r = 0.6$ and connect it with the convergence point for aromatic hydrocarbons by a straight line. Read the value of thermal conductivity at $T_r = 0.506$ (120°F.).

$$k = 0.0689 \text{ B.t.u./(hr./sq. ft.)(°F./ft.)}$$

The observed value at the same temperature is 0.0688 B.t.u./(hr./sq. ft.)(°F./ft.).

ILLUSTRATION 2. Calculate the thermal conductivity of 3-heptanone at 140°F.

Data: T_c = 1058°R. (estimated from the boiling point)
Effective number of carbon atoms $x = n - 2 = 7 - 2 = 5$
Structural contribution (Table 2) −0.0041

In Figure 2 locate the reference point for pentane, at $T_r = 0.6$, 0.0738. Subtract −0.0041 and locate new point, 0.0697. Connect the new point with the convergence point for ketones by a straight line. Read the value of thermal conductivity at $T_r = 0.566$ (140°F.)

$$k = 0.0742 \text{ B.t.u./(hr./sq. ft.)(°F./ft.)}$$

The observed value at the same temperature is 0.0747 B.t.u./(hr./sq. ft.)(°F./ft.).

This method of correlation was used to predict the thermal conductivity of the liquids tested in this investigation. The average deviation of the calculated from the observed values of thermal conductivity for a total of seventy-seven liquids (Parts I and III) is ±1.3%. The maximum deviation is about ±6.0%. The method of correlation was tested with respect to both the thermal conductivity and its temperature coefficient.

Correlation Based on Theoretical Equation

An equation, based on a simplified model of liquid state, for predicting the thermal conductivity of pure organic liquids and its temperature coefficient has been derived (Part II) and tested on a large number of straight-chain and branched liquids. Methods were also given for predicting the variables involved where no data are available (*11, 12*).

The equation is applicable to both normal and associated liquids. The only assumption involved in its derivation is a particular molecular arrangement in the liquid, which is in agreement with conclusions reached from X-ray diffraction studies. The equation is

$$k = C_p U_s \rho L \qquad (1)$$

where

C_p = specific heat at constant pressure, B.t.u./(lb.)(°F.)
U_s = velocity of sound in the liquid, ft./hr.
ρ = liquid density, lb./cu. ft.
L = available intermolecular distance, ft.
k = thermal conductivity of liquid, B.t.u./(hr./sq. ft.)(°F./ft.)

In the calculation of the available intermolecular distance L for chain compounds, the assumption is made that the molecules, like rods in a bundle, are

---

*For the first members of the high-polarity series, such as methyl alcohol, the reference point is 0.1120 B.t.u./(hr./sq. ft.)(°F./ft.) at $T_r = 0.6$.

TABLE 4

COMPARISON OF SOME EXPERIMENTAL VALUES OF THERMAL CONDUCTIVITY WITH VALUES CALCULATED BY THEORETICAL EQUATION AT 68°F.

Liquid	$k_{obs.}$, B.t.u./ (hr./sq. ft.) (°F./ft.)	C_p, B.t.u./ (lb.)(°F.)	U_s, ft./ sec.	ρ, lb./ cu. ft.	$L \times 10^{-9}$, ft.	$k_{calc.}$, B.t.u./ (hr./sq. ft.) (°F./ft.)	% Dev.
Cyclopentane	0.0764	0.428	4290*	46.50	0.257	0.0790	+3.41
Methyl cyclopentane	0.0698	0.446	3980*	46.60	0.236	0.0703	+0.72
Cyclohexane	0.0719	0.442	3740*	48.50	0.252	0.0726	+0.97
Methyl cyclohexane	0.0660	0.442	3583	47.90	0.251	0.0685	+3.79
Cyclohexene	0.0785	0.429	3920*	50.50	0.251	0.0767	−2.29
Cyclohexanone	0.0859	0.433	4731	59.00	0.190	0.0827	−3.72
i-Propyl benzene	0.0758	0.388*	4365*	53.70	0.236	0.0772	+1.84
n-Butyl benzene	0.0796	0.403*	4430*	53.60	0.236	0.0813	+2.14

*Estimated values.

aligned perpendicular to the direction of heat flow.

The equation will be applied here to ring compounds. The available intermolecular distance for ring compounds is calculated on the assumption that the rings are stacked like coins with their longest dimension perpendicular to the direction of heat flow. As an example the benzene molecule will be considered. The thickness of the ring as determined by X-ray diffraction measurements (*11*) is 5.3 Å. = 1.738×10^{-9} ft. For purposes of calculation the shape of the ring will be taken as a square. The size of the edge can then be calculated readily from the critical density and the ratio of critical molecular volume and volume at absolute zero. For benzene:

$$v_c = 15.1 \times 10^{-27} \text{ cu. ft.}$$

$$v_c/v_0 = 3.94$$

$$v_0 = 3.83 \times 10^{-27} \text{ cu. ft.}$$

$$d = \left(\frac{v_0}{t}\right)^{1/2} = 1.485 \times 10^{-9} \text{ ft.}$$

The benzene ring then appears as a short parallelopiped with its thickness as the longer dimension. Hence the rings will be stacked with their thickness perpendicular to the direction of heat flow. The procedure for evaluating the available intermolecular distance for ring compounds is

1. Obtain v_c, v
2. Calculate v_c/v_0 and v_0
3. Obtain t [X-ray diffraction data (*5*)]
4. Calculate d and X
5. $L = X - d$

The necessary equations for obtaining these data are

$$v_c = \frac{M}{\rho_c \times 2.73 \times 10^{26}} \qquad (2)$$

M = molecular weight
ρ_c = critical density, lb./cu. ft.
v_c = critical molecular volume, cu. ft.

$$v = \frac{M}{\rho \times 2.73 \times 10^{26}} \qquad (3)$$

ρ = density at 68°F., lb./cu. ft.
v = molecular volume at 68°F., cu. ft.

$$n = \frac{v_c}{v_0} = 2\left\{1 + \frac{(\rho_{f/2} - \rho_c)(T_c)}{(\rho_c)(T_c - T_f)}\right\} \qquad (4)$$

ρ_f = density at freezing point, lb./cu. ft.
v_0 = molecular volume at absolute zero, cu. ft.
T_c = critical temperature, °R.
T_f = freezing point, °R.

$$v_0 = \frac{v_c}{n} \qquad (5)$$

$$d = \left(\frac{v_c}{t}\right)^{1/2} \qquad (6)$$

t = thickness of ring, ft. (Figure 3)
d = molecular width at absolute zero, ft. (Figure 3)

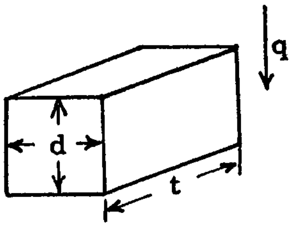


Fig. 3. Molecular model for simple ring compounds.

$$x = \left(\frac{v}{t}\right)^{1/2} \qquad (7)$$

X = molecular width at 68°F., ft.

$$L = X - d \qquad (8)$$

The correction for isomerization in the ratio n used for chain compounds is not necessary here. This method of evaluating the available intermolecular distance assumes that there is little or no empty space between molecules lined end to end or that the t dimension is the same at all temperatures. The same idea was used for chain compounds where the molecular length (equivalent to t here) l was taken as constant.

This method of evaluating the available intermolecular distance is strictly applicable to simple ring molecules such as benzene, cyclopentane, etc. The presence of side carbon atoms introduces a complication. When the side chain is long enough, the question arises whether to consider the molecule as a ring or a chain. The problem is solved readily by considering the molecule first as a simple ring, that is, evaluating the side chain as an equivalent ring width, then as simple chain, that is, evaluating the ring as an equivalent chain length. The correct intermolecular distance is obtained by calculating a weighted average of the two. In taking the average the following dimensions are necessary.

Ring	Thickness, t, ft.
Benzene	1.485×10^{-9}
Cyclopentane	1.494×10^{-9}
Cyclohexane	1.588×10^{-9}

Chain	Incremental length
$—CH_2—$ or $—CH_3$	0.300×10^{-9} ft.

The method of calculation will be illustrated by an example.

ILLUSTRATION 3. Calculate the thermal conductivity of *n*-butyl benzene at 68°F.

Data:

M = 134.21
T_c = 1190°R.
T_f = 334°R.
ρ = 53.60 lb./cu. ft. at 68°F.
ρ_f = 59.00 lb./cu. ft. at T_f [estimated by Watson's relation (*14*)]
ρ_c = 16.78 lb./cu. ft. at T_c
U_s = 4,430 ft./sec. at 68°F. [estimated by method given in (*11*)]
C_p = 0.403 B.t.u./(lb.)(°F.) at 68°F. [estimated by method given in (*12*)]

Consider molecule as a ring.

t = 5.30 Å. (for benzene ring) + 0.42 Å. (for side chain) = 5.72 Å. (*11*)
t = 1.876×10^{-9} ft.

$$n = v_c/v_0$$

$$= 2\left\{1 + \frac{(29.50 - 16.78)}{16.78}\left(\frac{1{,}190}{856}\right)\right\}$$

$$= 4.108 \qquad (4)$$

$$v_c = \frac{134.21}{2.73 \times 10^{26} \times 16.78}$$

$$= 29.30 \times 10^{-27} \text{ cu. ft.} \qquad (2)$$

$$v_0 = \frac{29.30 \times 10^{-27}}{4.108}$$

$$= 7.132 \times 10^{-27} \text{ cu. ft.} \qquad (5)$$

$$d = \left(\frac{7.132 \times 10^{-27}}{1.876 \times 10^{-9}}\right)^{1/2}$$

$$= 1.951 \times 10^{-9} \text{ ft.} \qquad (6)$$

$$v = \frac{134.21}{2.73 \times 10^{26} \times 53.60}$$

$$= 9.172 \times 10^{-27} \text{ cu. ft.} \qquad (3)$$

$$X = \left(\frac{9.172 \times 10^{-27}}{1.876 \times 10^{-9}}\right)^{1/2}$$

$$= 2.211 \times 10^{-9} \text{ ft.} \qquad (7)$$

$$L = (2.211 - 1.951) \times 10^{-9}$$

$$= 0.260 \times 10^{-9} \text{ ft.} \qquad (8)$$

Consider molecule as a chain (*11*).

$X = 1.771 \times 10^{-9}$ ft. [for straight-chain hydrocarbons (*11*)] (molecular length)

$$l = \frac{v}{X^2} = \frac{9.172 \times 10^{-27}}{(1.771 \times 10^{-9})^2}$$

$$= 2.924 \times 10^{-9} \text{ ft.}$$

$$d = \left(\frac{v_0}{l}\right)^{1/2} = \left(\frac{7.132 \times 10^{-27}}{2.924 \times 10^{-9}}\right)^{1/2}$$

$$= 1.562 \times 10^{-9} \text{ ft.}$$

$$L = X - d$$

$$= (1.771 - 1.562) \times 10^{-9}$$

$$= 0.209 \times 10^{-9} \text{ ft.}$$

Weighted average available intermolecular distance

Thickness of ring	1.485×10^{-9}
Length of chain $4 \times 0.300 \times 10^{-9}$	$= 1.200 \times 10^{-9}$
	2.685×10^{-9} ft.

Contribution of ring = $1.485 \times 0.260 \times 10^{-9}/2.685$	$= 0.1438 \times 10^{-9}$
Contribution of chain = $1.200 \times 0.206 \times 10^{-9}/2.685$	$= 0.0921 \times 10^{-9}$
Weighted average available intermolecular distance	0.2359×10^{-9} ft.

Thermal conductivity

$$k = C_p U_s \rho L \qquad (1)$$

$k = 0.403 \times 4{,}430 \times 3{,}600 \times 53.60 \times 0.236 \times 10^{-9} = 0.0813$ B.t.u./(hr./sq. ft.) C°F./ft.)

The observed value at the same temperature is 0.0796 B.t.u./(hr.)(sq. ft.)(°F./ft.). The temperature coefficient of thermal conductivity may be estimated by the method given in Part II. It can also be estimated as follows. Locate the calculated value of conductivity at 68°F. on Figure 2. Estimate the critical density of the liquid and locate convergence point. Connect the two points by a straight line.

This method of correlation was used to predict the thermal conductivity of the ring compounds tested in this investigation. The results are presented in Table 4. The average deviation of the calculated from the observed values of thermal conductivity for a total of fifty liquids, chain and ring compounds, is ±2.6%. The maximum deviation is about ±6.0%. This method of calculation is more tedious than the method based on the modified theory of corresponding states. However, it has the advantage that it requires no experimental data on thermal conductivity. A better example of its usefulness would be its application to the case of 1.2-bis (2-methoxy ethoxy) ethane, which is polyether. The compound is relatively new, and few data are available on its properties. Further, it cannot be classified into any of the types of liquids so far studied. Consequently the theoretical method is required. All the necessary data have to be estimated.

$M = 178.22$	$\rho_c = 19.67$ lb./cu. ft.
$T_b = 882.2$°R.*	$\rho_f = 63.6$ lb./cu. ft.*
$T_c = 1194$°R.*	$U_s = 4{,}100$ ft./sec.*
$T_f = 460$°R.*	$C_p = 0.498$ B.t.u./(lb.)(°F.)*

---

*Estimated values.

The only property that could not be estimated with the required accuracy was the density at 68°F. Actual measurements on the compound gave a value of 61.50 lb./cu. ft. The result is

$k = 0.0973$ B.t.u./(hr./sq. ft.)(°F./ft.) calculated

$k = 0.0987$ B.t.u./(hr./sq. ft.)(°F./ft.) observed

In view of the errors introduced by the necessity of estimating all but one of the required variables, the observed deviation is satisfactory.

SUMMARY

Observed values of thermal conductivity and temperature coefficients are presented for thirty-five pure organic liquids, in addition to those reported in Part I. Values of thermal conductivity or temperature coefficients for twenty-eight of these liquids have not been previously reported.

The experimental results were correlated by two previously proposed methods. The method based on a theoretical equation, previously used for chain compounds (Part II), was adapted here for calculations on cyclic compounds. The method based on a modified statement of the theory of corresponding states (Part I) was extended to cover the new types of organic compounds studied in this investigation.

The thermal conductivity of three liquids was observed to vary linearly with temperature up to about the boiling point, at 1 atm., of the liquids. In the region close to the freezing point, it was observed, for the higher n-paraffins, that the thermal conductivity ceases to be a linear function of temperature. The temperature coefficient of thermal conductivity approaches zero as the freezing point is approached. A transition temperature or region within the liquid state was observed and identified with the onset of molecular rotation.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of George Linder, a research fellow, who performed part of the experimental work.

This research was conducted under National Science Foundation Grants G-221 and 558. The Department of Chemical Engineering and the Engineering Experiment Station provided additional funds and facilities.

NOTATION

C_p = specific heat at constant pressure, B.t.u./(lb.)(°F.)
d = molecular diameter at absolute zero, ft.
k = thermal conductivity, B.t.u./(hr./sq. ft.)(°F./ft.)
L = mean available intermolecular distance, surface to surface, ft.
l = molecular length, ft.
M = molecular weight
n = number of carbon atoms in molecule, ratio of critical to minimum molecular volume
q = heat flow
T, t = temperature, °R., °F.
t = molecular thickness, ring compounds, ft.
U_s = velocity of sound in liquid, ft./sec.
v = molecular volume at given temperature, cu. ft.
X = molecular diameter at given temperature, ft.
x = effective number of carbon atoms

Greek Symbols

ρ = density, lb./cu. ft.

Subscripts

b = boiling point
c = critical
f = freezing point
0 = absolute zero
r = reduced

LITERATURE CITED

1. Baker, W. O., and C. P. Smyth, *J. Am. Chem. Soc.*, **60**, 1229 (1938).
2. Crowe, R. W., and C. P. Smyth, *ibid.*, **73**, 5401 (1951).
3. Fontana, B. J., *J. Phys. Chem.*, **57**, 222 (1953).
4. Hoffman, J. D., *J. Chem. Phys.*, **20**, 541 (1952).
5. Hoffman, J. D., and B. F. Decker, *J. Phys. Chem.*, **57**, 520 (1953).
6. Moore, R. J., P. Gibbs, and H. Eyring, *ibid.*, **57**, 172 (1953).
7. Sakiadis, B. C., and Jesse Coates, *Louisiana State Univ. Eng. Exp. Sta. Bull. No. 34*, Baton Rouge (1952).
8. *Ibid.*, *No. 48* (1954).
9. *Ibid.*, *No. 45* (1954).
10. ———, *A.I.Ch.E. Journal*, **1**, 275 (1955).
11. *Ibid.*, p. 281.
12. *Ibid.*, **2**, 88 (1956).
13. Seyer, W. F., R. F. Patterson, and J. L. Keays, *J. Am. Chem. Soc.*, **66**, 179 (1944).
14. Watson, K. M., *Ind. Eng. Chem.*, **35**, 398 (1943).

Presented at A.I.Ch.E. Houston meeting