Studies of Thermal Conductivity of Liquids

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Part I

Values of thermal conductivity and temperature coefficients for fifty-three pure organic liquids, obtained with newly designed, extensively tested apparatus, are presented. For thirty-one of these liquids values of thermal conductivity or temperature coefficients have not been previously reported. The statistically determined maximum error in the presented values of thermal conductivity of liquids is ±1.50%.

A method of correlating the thermal conductivity of liquids based on a modified statement of the theory of corresponding states is presented. Group contributions to the thermal conductivity were calculated. The thermal conductivity of liquids was predicted by this method and the average deviation of the calculated from the observed values for forty-seven liquids is ±1.50%. The proposed method of correlation permits the calculation of the thermal conductivity of a series of liquids at any temperature from a single known value.

The thermal conductivity of liquids is an important physical property, the value of which is required in the solution of most heat transfer correlations. The accuracy of the various correlations predicting these heat transfer coefficients cannot be better than the accuracy with which the thermal conductivity is known. Until recently, nevertheless, the available data were scanty and of doubtful accuracy. During recent years considerable effort has been expended in the experimental determination of the thermal conductivity of various liquids, but little progress has been made toward developing an apparatus that yields dependable results.

This paper presents experimental results on fifty-three pure organic liquids obtained with a newly designed, extensively tested apparatus. The results are correlated on a semitheoretical basis from a modified statement of the theory of corresponding states. An alternative theoretical equation for predicting the thermal conductivity of liquids is given in Part II. The two methods of correlation are mutually supporting.

APPARATUS

The thermoconductimetric apparatus was described in detail in an earlier publication (*5*), where the results of a number of tests were also presented. The design features were decided upon as a result of previous experimental and theoretical studies (*4, 5*) on the various features of previously used apparatus.

The apparatus (Figure 1) is of the steady state type. In it the liquid layer is enclosed between two, 6-in.-diam. horizontal parallel steel bars and heated downward to eliminate convection currents. To establish isothermal surfaces, the top and bottom bars are heated and cooled respectively by large amounts of water drawn from and returned to constant-temperature baths. The water rate is great enough to eliminate much temperature change after the water circulates through the apparatus. Heat flows in series through the liquid layer and a 4-in.-thick steel bar. To improve the accuracy of measuring the heat flow, eighteen thermocouples were embedded in the steel bars in four layers at different positions from the center of the bars, and the heat flow was measured by means of the thermal conductivity of steel and the dimensions of the bar. The thermal conductivity of the piece of steel used in the apparatus was determined in a separate, specially constructed apparatus (*5*). Heat losses were minimized by enclosing the bars in a glass cylinder and providing thermal guarding. This feature also permitted visual observation of the liquid layer, the thickness of which can be varied and is measured by means of three micrometers. This makes it possible to study the presence and effects of heat transfer by radiation across the liquid layer. The steel bars were nickel and chrome plated, the metal surfaces in contact with the liquid layer being highly polished.

Method of Calculation. In this apparatus the thermal conductivity of the liquid may be calculated by two independent methods, an extrapolation method and an over-all-resistance-to-heat-flow method. The extrapolation method, used by most investigators, is based on the equation for heat conduction involving the temperature drop across the liquid layer which is obtained by extrapolation of the thermocouple readings to the metal-liquid boundaries. The equation for heat conduction is

$$k = \frac{q\, x_L}{A\, \Delta\, t_L} \tag{1}$$

This equation assumes that the surfaces are perfectly plane and that there are no surface effects of any kind. In practice this condition is simply not met. Even after careful plating and polishing, surface irregularities of about 0.0005 in. are common. They introduce a considerable error in thin-liquid-layer apparatus.

The over-all resistance to heat-flow method is based on calculating the resistance to heat flow due to the steel bars and the enclosed liquid layer. Hence

$$R_T = \frac{\Sigma\,(\Delta t)}{q} \tag{2}$$

where

$\Sigma(\Delta t)$ = over-all temperature drop due to liquid layer and a known thickness of steel bars
q = heat flow across liquid layer and bars
R_T = total resistance to heat flow (including effects due to surface irregularities and films)

$$R_T = R_S + R_L \tag{3}$$

and

$$R_S = \frac{x_S}{k_S\, A} \tag{4}$$

$$R_L = \frac{x_L}{k_L\, A} \tag{5}$$

where

R_S = resistance to heat flow due to steel bars alone (including effects due to surface irregularities and films)
R_L = resistance to heat flow due to liquid layer

The resistance to heat flow due to the steel bars alone, R_S, is determined by making a run with the bars in direct contact. Subtracting this resistance from the resistance determined for a given liquid thickness, R_T, gives the resistance due to the liquid layer alone, R_L, and the thermal conductivity of the liquid is calculated from Equation (5).

The over-all resistance method is considered more correct because it takes into account the effect of surface irregularities and films. It also makes it possible to study the presence and effects of any convection currents or other extraneous factors.

Precision of Measurements. The described apparatus was submitted to a number of tests to establish its accuracy and dependability. It was shown that, within the range of experimental conditions, heat transfer by radiation across the liquid layer is negligible with no absorption taking place. Evidence was also given to show the absence of convection currents in downward heating.

The described thermoconductimetric apparatus is used as a primary device. The experimentally determined maximum error in the value of thermal conductivity of liquids is ±1.50%, of which ±1.0% is a statistically calculated maximum uncertainty in the determined value of thermal conductivity of steel.

RESULTS

The experimental results are presented in Table 1. 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.

COMPARISON WITH LITERATURE VALUES

An extensive literature survey has been made (*3*, *6*) and values of thermal conductivity for numerous liquids have been collected, classified, and evaluated. The more dependable results fall mainly into two groups differing consistently by about 5%. The first group comprises the results of L. Riedel and H. L. Mason, determined with a similar type of thin-film apparatus in the period 1940 to 1954. They found low values of thermal conductivity and temperature coefficients. The second group comprises the results of O. K. Bates et al. and T. K. Slawecki, determined with a thick- and thin-film type of apparatus respectively in the period 1933 to 1953. Their values of thermal conductivity are somewhat higher than those of the first group.

A comparison of some values of thermal conductivity determined by the authors with values published by these two groups of investiga-

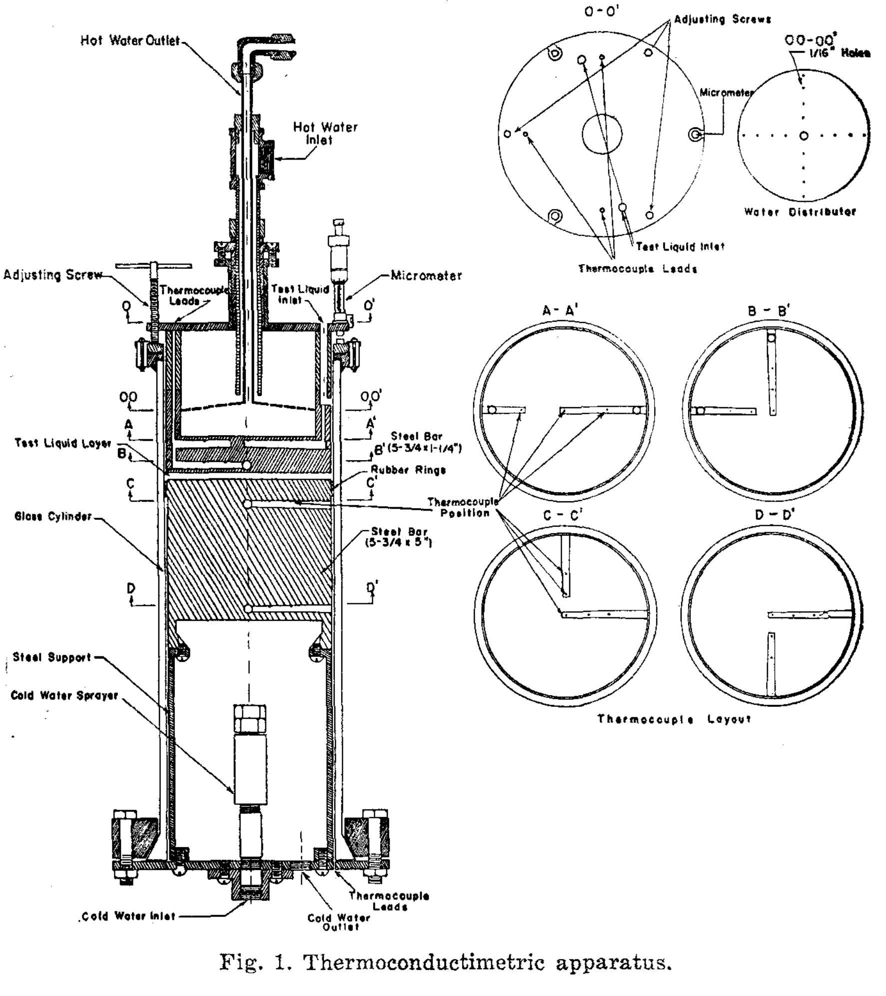

Fig. 1. Thermoconductimetric apparatus.

tors was made, and it was noted that the values of thermal conductivity of other investigators calculated by the extrapolation method (group 1) agree in general with the present authors' values calculated by the same method but are about 5% lower consistently than the values calculated by the correct over-all-resistance-to-heat-flow method. The difference is due to surface irregularities and films (5). This effect may be evaluated also from the over-all resistance of the bars when in direct contact. The presence of surface irregularities and films would increase the resistance to heat flow of the bars. Hence, it was found that if all the surface effects are due to surface irregularities, they are of the order of 0.0008 in. Since the metal surfaces were carefully machined, plated, and highly polished, at least to the same extent as in apparatus of other investigators, it is concluded that some of the best literature values of thermal conductivity are about 4 to 5% lower than the correct values.

The apparatus used by Bates et al. is a thick-film apparatus. The liquid-layer thickness was about 2 in., and the temperature drop across a given liquid-film thickness was determined by thermocouples placed within the liquid layer with their hot junctions located approximately 1/4 in. apart. The values obtained by Bates et al. agree well with the results of this investigation calculated by the correct over-all resistance method, which was to be expected as the liquid-film thickness is determined directly within the liquid layer and therefore is free of surface irregularities and films.

Although the results of T. K. Slawecki were calculated by the extrapolation method they agree with the authors' results calculated by the over-all-resistance-to-heat-flow method, probably because the liquid-layer thickness, in the apparatus used by Slawecki, was determined by electrical capacitance methods, which should give a true average value.

A comparison of the temperature coefficients of thermal conductivity for some liquids with literature values was made, and it was noted that the temperature coefficients of thermal conductivity determined in all thin-film types of apparatus are consistently lower than the values observed in this investigation; the values of Bates et al. are consistently higher.

TABLE 1.—OBSERVED VALUES OF THERMAL CONDUCTIVITY

Liquid	k at 100° F., B.t.u./(hr.) (sq. ft.) (°F./ft.)	$dk/dt \times 10^{-4}$ B.t.u./(hr.) (sq. ft.) (°F./ft.)/°F.	Temp. range, °F.	Source, purity*
n-Hexane	0.0714	−1.40	91–135	9a
n-Heptane	0.0725	−1.30	91–170	7b
n-Octane	0.0751	−1.15	93–170	9a
n-Nonane	0.0777	−1.30	92–171	9a
n-Decane	0.0770	−1.40	106–169	7b
n-Hexene-2	0.0715	−1.60	100–131	9c
n-Heptene-2	0.0747	−1.30	91–170	9a
n-Octene-2	0.0769	−1.40	92–171	9c
n-Octene-1	0.0740	−1.40	103–172	9c
2-Methyl pentane	0.0617	−1.00	87–121	9a
3-Methyl pentane	0.0628	−1.00	89–128	9a
2, 2-Dimethyl butane	0.0560	−0.93	85–110	9a
2, 3-Dimethyl butane	0.0592	−0.80	86–122	9a
2, 2, 4-Trimethyl pentane	0.0560	−1.05	101–171	9a
2, 2, 5-Trimethyl hexane	0.0623	−1.40	94–171	9a
Methyl alcohol	0.1187	−1.77	95–138	1b
Ethyl alcohol	0.0981	−1.20	95–167	10b
n-Propyl alcohol	0.0912	−0.95	95–168	6b
n-Butyl alcohol	0.0885	−1.02	94–170	1b
n-Amyl alcohol	0.0863	−0.91	94–170	5d
n-Hexyl alcohol	0.0878	−0.93	94–170	5d
n-Heptyl alcohol	0.0903	−0.81	95–169	5b
n-Octyl alcohol	0.0927	−1.00	95–170	7d
n-Decyl alcohol	0.0947	−1.18	95–170	5d
i-Propyl alcohol	0.0814	−0.95	94–171	8b
i-Butyl alcohol	0.0803	−0.81	94–170	5b
tert-Butyl alcohol	0.0670	−0.75	93–171	5b
Ethylene glycol	0.1510	+0.36	97–169	7b
Propylene glycol	0.1215	−0.35	96–169	4b
Glycerol	0.1789	+0.53	96–171	7b
Depropylene glycol	0.1007	−1.08	96–169	3c
Methyl acetate	0.0931	−1.92	96–120	7d
Ethyl acetate	0.0826	−1.62	106–145	6b
Propyl acetate (*n*-)	0.0796	−1.40	99–169	5b
Butyl acetate (*n*-)	0.0795	−1.26	98–170	7b
Amyl acetate (*n*-)	0.0782	−1.25	96–170	5b
Octyl acetate (*n*-)	0.0815	−1.45	104–170	2b
Methyl propionate	0.0849	−1.55	108–145	7b
Ethyl propionate	0.0800	−1.55	107–168	7b
Propyl propionate (*n*-)	0.0795	−1.34	108–170	5b
Amyl propionate (*n*-)	0.0790	−1.39	106–169	7b
Ethyl butyrate (*n*-)	0.0781	−1.38	107–169	5b
n-Amyl chloride	0.0676	−0.85	108–169	7b
1-Chlorodecane	0.0754	−1.23	106–169	5b
n-Propyl bromide	0.0571	−1.19	96–136	5b
n-Butyl bromide	0.0581	−1.13	103–170	5b
n-Amyl bromide	0.0599	−1.06	102–170	5b
n-Hexyl bromide	0.0614	−1.02	96–169	5b
n-Propyl iodide	0.0503	−0.90	105–170	5b
n-Heptyl iodide	0.0573	−0.98	102–169	5b
Nitromethane	0.1170	−1.97	110–168	5b
Nitroethane	0.0962	−1.55	108–168	5b
1-Nitropropane	0.0873	−1.44	110–169	5d

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1 Allied Chemical & Dye
2. Brothers Chemical
3. Carbide & Carbon
4. City Chemical
5. Eastman Kodak
6. Fisher Scientific
7. Matheson, Coleman & Bell
8. Merck
9. Phillips Petroleum
10. U.S. Industrial

a. Pure, 99 mole % min.
b. Reagent, research, Eastman-highest purity.
c. Technical, 95 mole % min.
d. Practical, 95–98%

The difference between the values observed in this investigation and those of Bates et al. is due to the effect of heat transfer by radiation across the liquid layer in the apparatus used by Bates, which amounted to about 7% of the heat flow by conduction. Bates did not

TABLE 2.—STRUCTURAL CONTRIBUTION TO THE THERMAL CONDUCTIVITY OF LIQUIDS AT $T_r = 0.6$

		dk, B.t.u./(hr.) (sq.ft.) (°F./ft.)
Aliphatic alcohols	$—OH$	—0.0070
Esters	$—C{\genfrac{}{}{0pt}{}{/\!\!/O}{\diagdown O—}}$	+0.0070*
Alkyl halides	$—Cl$	—0.0168
	$—Br$	—0.0248
	$—I$	—0.0310
Nitrated alkanes	$—NO_2$	0*
Isomerization		
	For 1 $—CH_3$group	—0.0060
	For 2 $—CH_3$ groups	—0.0104
	For 3 $—CH_3$ groups	—0.0142
Bonding		
	One double bond=	+0.0010
Effective Number of Carbon Atoms, x		
Aliphatic hydrocarbons	C_nH_{2n+2}	$x = n$
Aliphatic alcohols	$C_nH_{2n+1}OH$	$x = n$
Esters	$C_nH_{2n}O_2$	$x = n—2$
Alkyl halides	$C_nH_{2n+1}Cl$	$x = n$
	$C_nH_{2n+1}Br$	$x = n+1$
	$C_nH_{2n+1}I$	$x = n+2$
Nitrated alkanes	$C_nH_{2n+1}NO_2$	$x = n$

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*The first members of associated series such as alcohols and nitrated alkanes, have an abnormally high thermal conductivity; however, their relative values are consistent with the contributions given in Table 2. Hence any member of the alcohol series will differ from a corresponding member of the nitrate alkane series by 0.0070 B.t.u./(hr.) (sq.ft.) (°F|/ft.), including methyl alcohol and nitromethane. However methyl alcohol will differ by more than 0.0070 from the first member of the hydrocarbon series or methane.

correct for this heat transfer by radiation. Since for a given liquid-film thickness the heat transfer by radiation is greater for the higher or hotter section of the liquid layer than for the colder section, the calculated coefficient of thermal conductivity will be higher than the correct value, as noted. If the results obtained by Bates are corrected for the heat flow by radiation across the liquid layer, it will be found that the published values of thermal conductivity are about 0.8% high. The corrected values of the temperature coefficient agree in general with the values observed by the authors.

The low values of the temperature coefficient obtained with all thin-film apparatus are most probably due to the thermal expansion of the copper cylinders.

The accuracy of the results of this investigation, presented in Table 1, can also be shown indirectly by a comparison of the temperature coefficients for the homologue members of the alcohol series, which were fairly pure liquids. It will be noted that the temperature coefficients vary regularly from member to member, as expected. A plot of the temperature coefficients as a function of the number of carbon atoms was made, and a smooth curve drawn through the experimental points. The maximum deviation of any point from the curve was noted to be $\pm 0.08 \times 10^{-4}$ B.t.u./(hr.) (sq.ft.) (°F./ft.)/°F. For a temperature range of 74°F. covered in this investigation this corresponds to a maximum deviation of ±0.65% in the values of thermal conductivity, including the deviation due to any impurities in the liquids. The temperature coefficients for the same liquids determined by other investigators vary irregularly from liquid to liquid.

CORRELATION OF RESULTS

The basic conditions underlying the theory of corresponding states have been clearly stated(*2*). If all the conditions are met, it can be shown(*2*) that two systems should exhibit corresponding behavior if they are at the same reduced temperature and pressure or volume. Most liquids actually do not meet *all the* conditions; however, a corresponding-states behavior could arise under some other circumstances than those given, although the detailed behavior would be different.

Such a situation would arise when homologous members of the same series are considered. Hence the condition that all molecules should be spherically symmetrical could be changed to mean a group of nonspherical molecules having the same shape factor. This changes also the condition that the potential energy is a function only of intermolecular distance to a condition in which the potential energy has the same proportional dependence of potential on angular orientation. This permits the inclusion of polar substances. Finally the potential function may have a different shape, but it will be expected to vary uniformly.

The theory of corresponding states may then be stated on a broad basis in a different form. The same members of two different series will exhibit corresponding behavior to the same other members of their respective series, provided they are at the same reduced temperature and pressure. Since the effect of pressure on thermal conductivity is relatively small(*1*), the reduced pressure may be omitted from the correlation. Hence a plot of thermal conductivity as a function of number of carbon atoms, for the chain compounds, at the same reduced temperature should result in a family of curves of similar shape. Such a plot is shown in Figure 2. As predicted, the curves are parallel and have the same shape. The contribution to the thermal conductivity of a given functional group or atom in the molecule was determined by taking the hydrocarbon series as a basis and obtaining the difference between it and other series. These contributions are presented in Table 2.

It will be noted that the effective number of carbon atoms, *x*, is not the same for all series. It is clear that the size of the substituted atoms or functional groups, and the polarity of the molecule, which affect the shape factor and intermolecular forces, determine the value of *x*.

A theoretical equation for predicting the thermal conductivity of liquids will be derived in Part II. According to the theoretical equation

$$k = C_p U_s \rho L \tag{6}$$

Substituting an empirical equation for the velocity of sound in Equation (6) (Part II) results in

$$k = \frac{C_p R^3 \rho^4 L}{M^3} \tag{7}$$

Values of the variables involved at 68°F. for members of the hydrocarbon and alcohol series are tabulated (Table 3) for purposes of comparison.

It will be noted that the specific heat and the critical density are approximately constant for members of the same series; whereas the intermolecular distance, L, varies somewhat from member to member. At the critical temperature Equation (7) may be expressed as follows,

$$k = C\,Y \tag{8}$$

where

$C = C_p\,\rho_c^4$, group constant for a given series
$Y = R^3\,L/M^3$, group consisting of additive factors

If the small variations observed are neglected, the function Y may also be taken as a constant for a given series. Hence it may be predicted as a good approximation that at the critical temperature the thermal conductivity of a homologous series will be a constant and the same for all the members of the series. A plot of thermal conductivity of a given series as a function of reduced temperature, with the number of carbon atoms as a parameter, will result in a family of curves converging to a point at $T_r = 1.0$. Such a plot for the hydrocarbon series is shown in Figure 3. Only the last five members of the series were studied, the remaining members being used as a reference for the other series. It will be noted that, as expected, the convergence points for both the normal and associated liquids are arranged in the order of their relative critical densities. The method of calculation may be shown by an example.

Illustration. Calculate the thermal conductivity of *i*-butyl alcohol at 100.0°F.

Data: $T_c = 995.0°R.$

Effective carbon atom number $x = n = 4$
Structural contribution —OH +0.0070
1 Isomerization —0.0060
net +0.0010

In Figure 3 locate the reference point for butane, at $T_r = 0.6$, 0.0775. Add 0.0010 and locate new point, 0.0785. Connect the new point with the convergence point for alcohols by a straight line. Read the value of thermal conductivity at $T_r = 0.563$ (100.0°F.), $k = 0.0818$ B.t.u./(hr.)(sq.ft.)(°F./ft.). The observed value at the same temperature is 0.0803 B.t.u./(hr.)(sq.ft.)(°F./ft.).

TABLE 3

Liquid	C_p, B.t.u./(lb.)(°F.)	$L \times 10^{-9}$, ft.	ρ_c lb./cu.ft.
n-Hexane	0.534	0.268	14.49
n-Heptane	0.526	0.251	14.59
n-Octane	0.522	0.245	14.59
n-Nonane	0.521	0.230	14.59
Ethyl alcohol	0.575	0.259	17.20
n-Propyl alcohol	0.563	0.230	17.02
n-Butyl alcohol	0.563	0.217	16.95
n-Amyl alcohol	0.560	0.206	16.90

The ratio R/M has been calculated also for a few liquids:

Liquid	R/M
n-Hexane	0.369
n-Heptane	0.362
n-Octane	0.358
Ethyl alcohol	0.318
n-Propyl alcohol	0.318
n-Butyl alcohol	0.319
Methyl acetate	0.273
Ethyl acetate	0.280
n-Propyl acetate	0.285

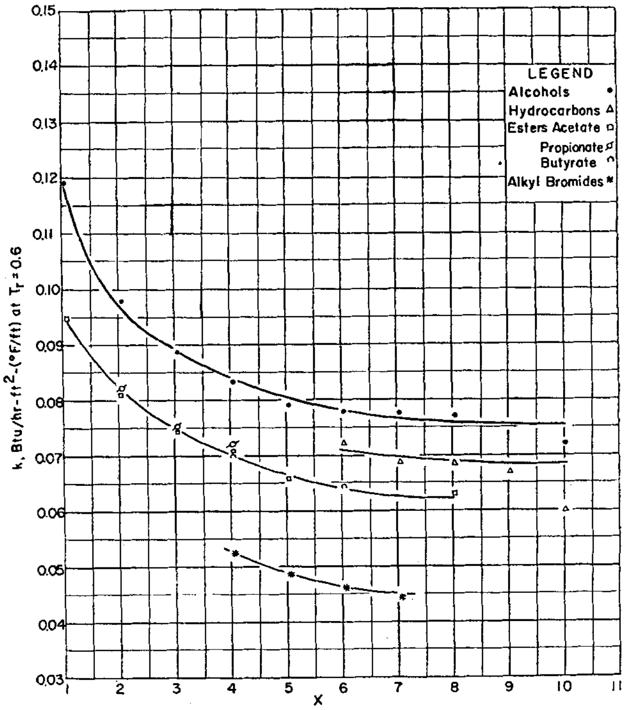

Fig. 2. Thermal conductivity vs. effective number of carbon atoms.

This method of correlation was used to predict the thermal conductivity of the liquids tested in this investigation. Representative results are presented in Table 4.

The average deviation of the calculated from the observed values of thermal conductivity for the forty-seven liquids is ±1.50%. The maximum deviation is about ±6.0%. Considering the purity of the liquids involved, the observed average deviation is satisfactory. It will be noted that the method of correlation was tested with respect both to the thermal conductivity and its temperature coefficient.

At any one temperature the thermal conductivity appears both to increase and to decrease with increasing molecular weight, as in the case of the hydrocarbons and aliphatic alcohols respectively. At the same reduced temperature, however, the thermal conductivity for all liquids decreases with molecular weight.

This method of correlation permits the calculation of the thermal conductivity of a series of liquids at any temperature from a single known value for one member. The convergence point may be established readily from its critical density. A straight line connecting the known experimental value with the convergence point will pass through the $T_r = 0.6$ point, the effective value of x being determined from the structure of the molecule. The value read at $0.6T_c$ and the effective value of x will establish the structural contribution of the functional group in the series. The thermal conductivity at any temperature, for any member of the series, is then readily determined. The required single value may be calculated from the theoretical equation presented in Part II, in which case no experimental data are needed.

SUMMARY

Observed values of thermal conductivity and temperature coefficients are presented for fifty-three pure organic liquids. Values of thermal conductivity or temperature coefficients for thirty-one of these liquids have not been previously reported. It is indicated that the best literature values of thermal conductivity are most probably low, on account of surface effects that were not considered in most investigations.

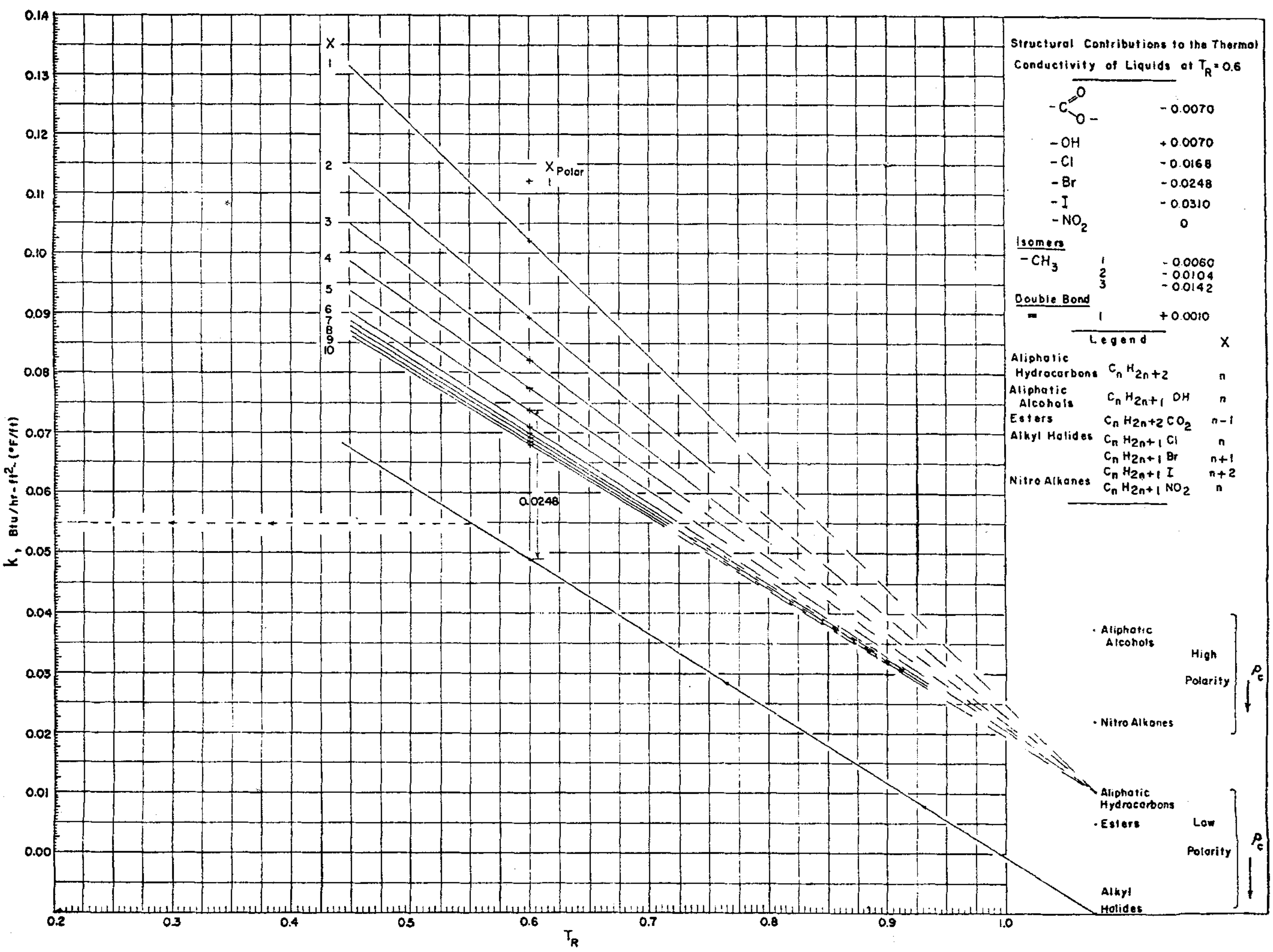

Fig. 3. Thermal conductivity of liquids vs. reduced temperature.

TABLE 4.—COMPARISON OF SOME EXPERIMENTAL VALUES OF THERMAL CONDUCTIVITY WITH VALUES CALCULATED BY CORRELATION BASED ON THE THEORY OF CORRESPONDING STATES

Liquid	T_c, °R.	T_r	$k_{calc.}$†	$k_{obs.}$†	% Dev.‡	T_r	$k_{calc.}$†	$k_{obs.}$†	% Dev.‡
n-Heptane	972.0	0.567	0.0738	0.0737	+0.14	0.648	0.0637	0.0634	+0.47
n-Nonane	1060.0*	0.520	0.0785	0.0787	+0.25	0.595	0.0691	0.0685	+0.87
Heptene-2	975.0*	0.565	0.0755	0.0759	−0.53	0.646	0.0651	0.0656	−0.61
n-Propyl alcohol	966.0	0.574	0.0922	0.0917	+0.54	0.650	0.0840	0.0847	−0.83
n-Hexyl alcohol	1102.0*	0.502	0.0867	0.0884	−1.92	0.571	0.0807	0.0813	−0.74
Methyl acetate	912.0	0.610	0.0935	0.0939	−0.43	0.635	0.0887	0.0893	−0.67
Amyl acetate (*n*-)	1090.0*	0.510	0.0782	0.0788	−0.76	0.578	0.0695	0.0695	0
Ethyl propionate	984.0	0.565	0.0807	0.0808	−0.12	0.635	0.0703	0.0699	+0.57
Ethyl butyrate (*n*-)	1020.0	0.555	0.0768	0.0771	−0.39	0.616	0.0683	0.0686	−0.44
1-Chlorodecane	1340.0*	0.422	0.0745	0.0747	−0.27	0.469	0.0683	0.0669	+2.10
n-Hexyl bromide	1210.0*	0.460	0.0613	0.0618	−0.81	0.520	0.0544	0.0544	0
n-Propyl iodide	1074.0*	0.526	0.0510	0.0498	+2.41	0.586	0.0445	0.0440	+1.13
Nitroethane	1004.0*	0.566	0.0945	0.0950	−0.52	0.625	0.0860	0.0857	+0.35
2-Methyl pentane	895.0	0.610	0.0637	0.0630	+1.11	0.650	0.0591	0.0596	−0.84
2, 2-Dimethyl butane	885.0	0.616	0.0590	0.0574	+2.78	0.644	0.0560	0.0551	+1.63
2, 2, 4-Trimethyl pentane	980.0	0.573	0.0575	0.0559	+2.86	0.644	0.0507	0.0486	+4.31
i-Butyl alcohol	995.0	0.555	0.0825	0.0808	+2.10	0.632	0.0757	0.0746	+1.47

*Estimated values. †k = B.t.u./(hr.)(sq. ft.)(°F./ft.) ‡Percentage deviation of calculated from observed values.

A method of correlating the thermal conductivity of liquids based on the theory of corresponding states has been developed and has been tested on a large number of liquids. The thermal conductivity of a series of liquids may be determined from one known value, at any one temperature, of one of its members.

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NOTATION

A = heat transfer area, normal to heat flow, sq.ft.
C_p = specific heat at constant pressure, B.t.u./(lb.) (°F.)
C = group of constants
k = thermal conductivity, B.t.u./(hr.) (sq.ft.) (°F./ft.)
L = mean available intermolecular distance, surface to surface, ft.
M = molecular weight, lb.
n = number of carbon atoms
q = rate of heat flow, B.t.u./hr.
R = resistance to heat flow, (°F.) (hr.) /B.t.u.
R = additive constant
T = absolute temperature, °R.
t = temperature, °F.
U_s = velocity of sound, ft./sec.
x = effective number of carbon atoms
x = thickness, ft.
Y = group of additive factors
ρ = density, lb./cu.ft.
Δt = temperature drop, °F.
$\Sigma(\Delta t)$ = over-all temperature drop, °F.

Subscripts

c = critical
L = liquid
r = reduced
S = steel
T = total

LITERATURE CITED

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Part II

An equation for predicting the thermal conductivity and its temperature coefficient of pure organic liquids has been derived on the basis of a particular molecular arrangement in the liquid. The equation is applicable to both normal and associated liquids. Detailed methods and tables are given in the Appendix for predicting the variables involved where no data are available. The equation has been tested on forty-two liquids, and the average deviation of the calculated from the observed values of thermal conductivity is ± 2.6%.

In Part I the values of thermal conductivity observed in this investigation were correlated on the basis of a modified statement of the theory of corresponding states. This method requires at least one experimental value. This part of the series presents the results of an attempt to derive without experimental information a simple theoretical equation for the prediction of thermal conductivity and its temperature coefficient.

The equation is derived on the basis of a particular molecular arrangement in the liquid, consistent with the results of X-ray diffraction studies in liquids. It has been tested on a large number of liquids (*see* Part I). The success of the equation in predicting the thermal conductivity of liquids, both normal and associated, justifies indirectly the assumptions made in its derivation and throws light on the mechanism of heat conduction in liquids.

PREVIOUS WORK

A number of equations, mostly empirical, for predicting the thermal conductivity of liquids have been presented. None of the theoretical equations appear to be satisfactory, as the predicted values of thermal conductivity vary widely from experimental data, and the empirical equations relating the thermal conductivity to other liquid properties are little better. The theory of the liquid state has not been developed to the point where a satisfactory equation for thermal conductivity may be arrived at without vitiating assumptions. An equation with as simplified a theoretical background as possible is therefore desirable.

One such equation was developed in 1923 by P. W. Bridgman(*1*), who assumed that the liquid molecules were arranged in a cubical lattice, at a distance d ft. apart, vibrating about centers,

$$d = \left(\frac{M}{N\rho}\right)^{1/3}$$

The total energy of a molecule was taken as $3RT/N$ ($3/2RT/N$ kinetic energy and $3/2RT/N$ potential energy), or $1/2RT/N$ for each degree of freedom. This was assumed to be propagated along a row of molecules with the velocity of sound U_s ft./sec. in the liquid. Bridgman obtained the equation

$$k = 3\frac{RU_s}{Nd^2}$$

B.t.u./(hr.) (sq. ft.) (°F./ft.)

Kardos(*8*) in 1934 modified Bridgman's equation to avoid specifying the amount of molecular energy. He considered an energy drop between adjacent molecular surfaces and substituted the distance L between the surfaces of adjacent molecules, instead of the distance d of their centers. He arrived by a reasoning similar to that of Bridgman at the following relation:

$$k = LU_s\rho C_p$$

The difficulty in using this equation lies in the finding of suitable values for the variables involved. Kardos suggested that as a first approximation L be assumed constant and equal to 3.12×10^{-10} ft.

The thermal conductivity of twenty-eight liquids was calculated by use of Bridgman's and Kardos' equations. The average deviation of the calculated from the observed values of thermal conductivity was found to be ±15 and ±23% respectively. The maximum deviation is ±40% and ±104% respectively; hence it would appear that the assumption of a constant L in Kardos' equation is not tenable if reasonably accurate values are required.

The theoretical equation proposed by Kardos will be interpreted on the basis of recent developments, and methods for determining the variables involved given. It will be shown that when the variables involved are properly evaluated the predicted values of thermal conductivity agree well with the values of thermal conductivity observed in this investigation.

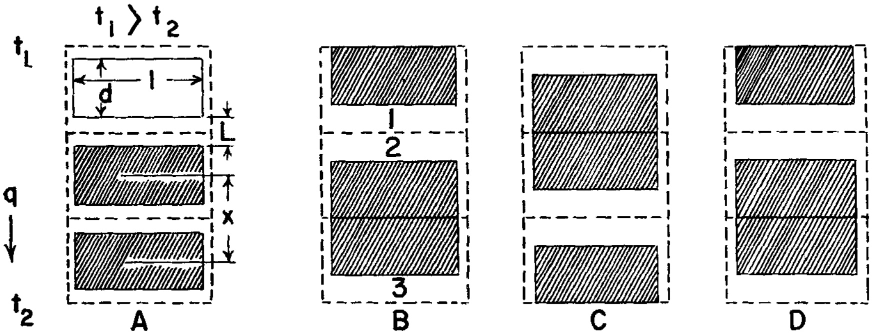

Fig. 1. Heat transfer mechanism with assumed molecular model.

The derivation of an equation for thermal conductivity requires the use of a model of the liquid state and the assumption of a mechanism of heat conduction. The model of liquid state considered here originates from the results of X-ray–diffraction studies of liquids.

BASIC CONCEPTS

The liquid state differs from the gas state in that the individual molecules are affected considerably by the presence of their neighboring molecules. It differs from the solid state in that the molecules have a certain degree of freedom on the macroscopic scale. The setting of a temperature gradient across a liquid layer should result in the formation of isothermal planes of liquid molecules having the same mean energy. This arrangement will cause the molecules to move in the direction of heat flow only. Owing to the large intermolecular forces existing in the liquid state, only a small fraction of the total energy is transferred by individual molecules over relatively long distances. The greater part of energy transfer takes place by the distant action of neighboring molecules, much in the same way that mechanical motion is transferred from point to point along a vibrating network of spheres connected by springs. Further, as a good approximation it can be assumed that on the average the energy transferred in a given time by a molecule moving freely in the direction of heat flow is equal to that transferred by a molecule vibrating about a mean position during the same time. This simplified model is substantially in agreement with the "cybotactic state" proposed by G. W. Stewart and coworkers(*17*) (*see also 14*) for isothermal conditions. G. W. Stewart attributes a "microcrystalline" structure to a liquid by assuming the presence of a large number of "cybotactic groups." These groups are not permanent and do not have sharp boundaries as in a crystal. Rather, over any appreciable time there are a greater number of these groups than of groups having completely disordered arrangement. The more elongated the molecule, as in a chain, the better the arrangement within the groups. The existence of a temperature gradient in a liquid layer should favor such an internal molecular arrangement.

In the case of a long-chain-hydrocarbon liquid, such as *n*-heptane (similar considerations apply to different-shaped molecules), the molecules in the liquid layer are oriented end to end on long chains in a two-dimensional pattern. The chains or layers repeat themselves throughout most of the liquid layer, some chains occasionally being disordered by molecules assuming different orientation; some groups may be broken up and new ones formed.

The process of heat conduction may be visualized as shown in Figure 1. In step *A* the molecules, represented by shaded rectangles, are in an assumed starting position. In step *B* molecule 1 moves toward a hotter molecule and molecules 2 and 3 move toward each other to collide. Molecule 1 on reaching the hotter molecule collides with it, picks up excess energy, and starts back. In step *C* molecule 1 collides with molecule 2, gives up its excess energy, and bounces back toward the hotter molecule again. In step *D* molecule 2 collides with molecule 3, giving up its newly gained excess energy. Steps *B* and *C* are repeated indefinitely. There is little or no lateral motion as adjacent molecules have the same mean absolute energy and the container walls are well insulated.

In Figure 1 the cross-sectional area of the molecules is represented as a rectangle, but no molecule has such sharp-edged boundaries. X-ray diffraction studies of the internal structure of molecules show that the carbon atoms in the molecule are arranged in a zigzag pattern at definite angles and distances apart, with the hydrogen atoms attached at definite positions in the chain. If each atom is visualized not as a point mass, but as distribution of charges in space, the molecule will appear like a rod with rough edges. The space occupied by this rod cannot be penetrated by any other molecule and represents the minimum volume or molecular volume at absolute zero v_o. For purposes of calculation it is easier to represent the minimum volume by a parallelopiped with height and width d equal to the diameter of the rod. The cross section of the molecule then may be represented by a rectangle, as in Figure 1.

At absolute zero the molar volume V_o is simply the sum of the minimum molecular volumes, or

$$V_o = \sum_{1}^{N} v_o \qquad (1)$$

As the temperature increases, the molecules begin to vibrate and the molar volume increases. The difference between the molar volume V at a given temperature and that at absolute zero is simply empty space within which the molecules move. As a consequence of the foregoing assumption that the molecules vibrate about fixed equilibrium positions, the available volume $V_a = V - V_o$ will be distributed around the minimum molecular volume, as shown in Figure 1 by dotted lines. It is clear therefore that according to the suggested mechanism of heat conduction, the significant intermolecular distance is the available distance between the molecular surfaces L and not the molecular diameter d.

DERIVATION OF EQUATION

An energy drop of

$$Q = -\left(\frac{dQ/N}{dx}\right)L = -L\left(\frac{dQ/N}{dT}\right)\frac{dT}{dx} \qquad (2)$$

per molecule along a row of molecules in the direction of heat flow, where $x = d + L$, may be considered. If it is assumed that heat is transmitted through the liquid with a velocity equal to the velocity of sound in the liquid U_s, the total energy, passing a fixed point in a row of molecules per unit time, is the product of the energy difference and the number of steps contained in a row U_s ft. long, or

TABLE 1.—COMPARISON OF SOME EXPERIMENTAL VALUES OF THERMAL CONDUCTIVITY WITH VALUES CALCULATED BY THEORETICAL EQUATION (8) 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.*
n-Heptane	0.0767	0.526	3786	42.60	0.253	0.0773	+0.8
n-Amyl alcohol †	0.0892	0.560	4111	50.70	0.218	0.0916	+2.7
Octene-2	0.0814	0.503 ‡	3973 ‡	45.00	0.249	0.0806	−1.0
n-Octyl acetate	0.0861	0.485 ‡	4240	54.20	0.207	0.0831	−3.6
Ethyl propionate	0.0850	0.457	3940 ‡	55.50	0.239	0.0860	+1.2
Ethylene glycol	0.1498	0.575	5490	69.40	0.181	0.1428	−4.9
Glycerol	0.1772	0.570	6249	78.60	0.172	0.1734	−2.2
2, 2-Dimethyl butane	0.0590	0.518	3320 ‡	40.45	0.231	0.0579	−1.9
i-Propyl alcohol	0.0844	0.596	3900	49.00	0.214	0.0877	+3.9
n-Amyl bromide	0.0633	0.295 ‡	3720 ‡	75.90	0.207	0.0621	−1.9
n-Propyl iodide	0.0532	0.205 ‡	3190 ‡	109.00	0.210	0.0539	+1.3
n-Amyl chloride	0.0703	0.440 ‡	3885 ‡	55.00	0.216	0.0731	+4.0

*Percentage of deviation of calculated from observed values of thermal conductivity.

†For methyl and ethyl alcohol, nitromethane and nitroethane, the molecular length is much smaller than the diameter, and a different molecular arrangement becomes necessary.

‡Estimated values.

$$-L\left(\frac{dQ/N}{dT}\right)\left(\frac{dT}{dx}\right)\left(\frac{U_s}{x}\right)$$

The total energy transfer across unit area is the product of the energy transfer across a single row and the number of rows in unit cross section, or

$$\frac{q}{A} = -L\left(\frac{dQ/N}{dT}\right)\left(\frac{U_s}{x}\right)$$

$$\left(\frac{dT}{dx}\right)\frac{1}{(yz)} \qquad (3)$$

where yz = cross-sectional area corresponding to the dimension x.

The equation for heat conduction per unit area is stated as

$$\frac{q}{A} = -k\frac{dT}{dx} \qquad (4)$$

Substituting Equation (3) in (4) and solving for thermal conductivity results in

$$k = \left(\frac{dQ/N}{dT}\right)\left(\frac{L}{x}\right)\frac{1}{(yz)}U_s \qquad (5)$$

as by definition

$$\left(\frac{dQ/N}{dT}\right)_p = \frac{MC_p}{N} \qquad (6)$$

where M = molecular weight, lb.
C_p = specific heat at constant pressure. B.t.u./(lb.) (°F.)

Also the molecular volume v is

$$yzx = \frac{M}{\rho N} \qquad (7)$$

where ρ = liquid density, lb./cu.ft. Substituting Equations (6) and (7) in (5) and canceling terms results in

$$k = C_p\,U_s\,\rho\,L \qquad (8)$$

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.)

The significance of the intermolecular distance L will be shown by consideration of *n*-heptane.

n-Heptane at 68°F.

Data. $k = 0.0767$ B.t.u./(hr.) (sq. ft.) (°F./ft.), value observed in this investigation
$C_p = 0.526$ B.t.u./(lb.) (°F.)
$\rho = 42.60$ lb./cu.ft.
$U_s = 1.364 \times 10^7$ ft./hr.

Substituting the given data in Equation (8) and solving for L results in

$$L = 0.251 \times 10^{-9}\text{ ft.}$$

X-ray–diffraction studies by G. W. Stewart and coworkers have shown that the diameter of the heptane molecule at about 68°F. is 1.77×10^{-9} ft. (5.40 Å.) This diameter actually corresponds to the dimension x shown in Figure 1, or

$$d + L = 1.77 \times 10^{-9}\text{ ft.}$$

It was stated above that the molecular volume for heptane may be taken as a parallelopiped, or

$$V = \sum_{1}^{N} v \qquad (9)$$

and

$$v = \frac{M}{\rho N} = (d + L)\,yz \qquad (7a)$$

where, as

$$z = x = d + L$$

$$v = (d + L)^2 y \qquad (7b)$$

Substituting values in Equation (7*a*) results in

$$v = \frac{100.20}{42.6 \times 2.73 \times 10^{26}} =$$

$$8.61 \times 10^{-27}\text{ cu. ft.}$$

and

$$y = \frac{8.61 \times 10^{-27}}{(1.77 \times 10^{-9})^2} =$$

$$2.752 \times 10^{-9}\text{ ft.}$$

It will be shown in the Appendix that the dimension y is actually equal to the molecular length l, or in other words there is no available volume between the ends of the molecules in a given layer, as if the molecules were arranged in a long continuous chain. If the intermolecular distance L is the only available distance, it should be possible to calculate the minimum molecular volume at absolute zero as follows:

$$v_o = d^2\,1 \qquad (10)$$

Hence

$$d = 1.77 \times 10^{-9} - 0.251 \times 10^{-9} =$$

$$1.519 \times 10^{-9}\text{ ft.}$$

$$v_o = \left(1.519 \times 10^{-9}\right)^2\left(2.752 \times 10^{-9}\right) =$$

$$6.35 \times 10^{-27}\text{ cu. ft}$$

If the density at absolute zero is available, the obtained answer can be checked; however, the results can be checked by a different method if the critical density is known. For *n*-heptane, $\rho_c = 14.58$ lb./cu.ft. The critical volume is next calculated by Equation (7), or

$$v_c = \frac{100.20}{14.58 \times 2.73 \times 10^{26}} = 25.2 \times 10^{-27} \text{ cu. ft.}$$

The ratio of the critical volume to the volume at absolute zero is

$$m = v_c/v_0 = \frac{25.2 \times 10^{-27}}{6.35 \times 10^{-27}} = 3.965$$

It is important to note that according to van der Waals' equation

$$v_c = 3v_0$$

Further it is found experimentally that v_c is more nearly equal to $4v_0$ than $3v_0$, in agreement with the value calculated above.
Berthelot's equation gives

$$v_c = 4v_0.$$

It is clear then that, if the ratio of the critical volume to the volume at the absolute zero is known, the thermal conductivity of a liquid can be calculated by reversing the illustrated procedure. For the case of *n*-heptane the ratio *m* was calculated by a method given in the Appendix and found to be equal to 3.98. By use of this value of *m*, the thermal conductivity of *n*-heptane was found to be 0.0773 B.t.u./(hr.) (sq.ft.) (°F./ft.), or 0.8% higher than the observed value.

It should be emphasized that the value of *L* will vary from liquid to liquid and is a function of temperature, becoming zero at the absolute zero. Kardos erroneously assigned a constant value to it.

Methods of calculating the variables involved in Equation (8) are given in the Appendix.

COMPARISON WITH EXPERIMENTAL VALUES

Equation (8) was used to predict the thermal conductivity of the liquids used in this investigation (*16*). The variables involved were calculated by the methods outlined in the Appendix. Representative results are shown in Table 1.

In the calculation of the thermal conductivity of isomers it was noted that a systematic deviation occurred. This was corrected as follows.

For isomers where $n = 1$, $v_c/v_o = v_c/v_o$ [Equation (20)]—0.23. (*See* Appendix, Table 4.)

For higher values of *n* the correction is probably 0.23*n*, but there are no substantiating data available. The average deviation of the calculated from the observed values of thermal conductivity for forty-two liquids was found to be ±2.6%. The maximum deviation was about ±6%. Considering the errors introduced by the necessity for estimating two or more variables for some liquids, and the purity of the liquids involved, the observed average deviation is satisfactory. The method of calculation is shown by an example:

ILLUSTRATION 1. Calculate the thermal conductivity of propyl acetate at 68°F.

Data $C_p = 0.459$ B.t.u./(lb.) (°F.)
$\rho = 55.40$ lb./cu.ft.
$T_c = 988.5$°R.
$M = 102.13$
$U_s = 3912$ ft./sec.
$\rho_c = 18.42$ lb./cu.ft.
$T_f = 321.0$°R.

Calculation of ratio of critical to minimum molecular volume, $\mathbf{v}_c/\mathbf{v}_o$

$$\rho_o/\rho_c = 2\left\{1 + \left(\frac{\rho_f/2 - \rho_c}{\rho}\right)\left(\frac{T_c}{T_c - T_f}\right)\right\} \tag{20}$$

$$\rho_f = \frac{\omega_f}{\omega_{68°\text{F.}}}\,\rho_{68°\text{F.}}$$

$$\omega_f = 0.1473 \text{ [Eq. (22)]}$$

$$\omega_{68°\text{F.}} = 0.1298 \text{ [Eq. 22)]}$$

$$\rho = 62.95 \text{ lb./cu. ft.}$$

$$\rho_o/\rho_c = 2\left\{1 + \left(\frac{62.95/2 - 18.42}{18.42}\right)\left(\frac{988.5}{988.5 - 321.0}\right)\right\} \quad \rho_o/\rho_c = 4.09$$

No correction for isomerization.

Calculation of minimum molecular volume, $\mathbf{v}_0$

$$v_o = v_c/4.09$$

$$v_c = \frac{M}{\rho_c N} = \frac{102.13}{2.73 \times 10^{26} \times 18.42} = 20.3 \times 10^{-27} \text{ cu. ft.}$$

$$v_o = 20.3 \times 10^{-27} / 4.09 = 4.952 \times 10^{-27} \text{ cu. ft.}$$

Calculation of intermolecular length, L

$$v = x^2 1 = \frac{M}{\rho N}$$

$$x = 5.03\text{Å.} = 1.650 \times 10^{-9} \text{ ft.}$$

(Table 4)

$$1 = \frac{M}{\rho N x^2} = 2.480 \times 10^{-9} \text{ ft.}$$

$$d = \left(\frac{v_o}{1}\right)^{\frac{1}{2}} = \left(\frac{4.952 \times 10^{-27}}{2.480 \times 10^{-9}}\right)^{\frac{1}{2}} = 1.415 \times 10^{-9} \text{ ft.}$$

$$L = x - d$$

$$L = (1.650 - 1.415) \times 10^{-9} = 0.235 \times 10^{-9} \text{ ft.}$$

Calculation of thermal conductivity, k

$$k = C_p U_s \rho L \tag{8}$$

$k = (0.235 \times 10^{-9})$ (0.459) (55.40) (3912×3600)
$k = 0.0841$ B.t.u./(hr.) (sq.ft.) (°F./ft.)

The observed value is 0.0841 B.t.u./(hr.) (sq.ft.) (°F./ft.)

TEMPERATURE COEFFICIENT OF THERMAL CONDUCTIVITY

The thermal conductivity of a liquid at a temperature other than 68°F. can be predicted by substituting the appropriate values for the specific heat, velocity of sound, and density. The intermolecular distance increases somewhat with increasing temperature, but not so much as would be expected from corresponding density changes. Since the coefficient of thermal expansion for many liquids is about the same, the effect of temperature on the intermolecular distance was determined for a few liquids from the known thermal conductivity, and the result applied to other liquids. It was found that

$$\frac{dL}{dt} = 0.0055 \times 10^{-11} \text{ ft./°F.} \tag{11}$$

Calculated and observed temperature coefficients of thermal conductivity for a few liquids, for which reliable values of the properties involved are available, are presented in Table 2.

TABLE 2.—CALCULATED AND OBSERVED TEMPERATURE COEFFICIENTS OF THERMAL CONDUCTIVITY $dk/dt \times 10^{-4}$, B.t.u. / (hr.) (sq.ft.) (°F./ft.) / °F.

Liquid	Calculated*	Observed
n-Hexane	−1.39	−1.40
n-Heptane	−1.44	−1.30
n-Octane	−1.22	−1.15
n-Propyl alcohol	−0.78	−0.95
n-Amyl alcohol.	−0.78	−0.91
Ethyl acetate...	−1.22	−1.62
2-Methyl pentane	−1.05	−1.00
2, 2, 4-Trimethyl hexane	−1.17	−1.05
Glycerol	+1.00	+0.53
Ethylene glycol.	+0.27	+0.36

*The effect of temperature on the intermolecular distance was estimated by Equation (11).

The calculated and observed temperature coefficients agree fairly well. The coefficients for ethylene glycol and glycerol are positive owing to the small negative temperature coefficient of the velocity of sound.

Since the density, velocity of sound, and specific heat vary linearly with temperature at temperatures sufficiently removed from the melting point, it will be expected that in this region the thermal conductivity will also vary linearly with temperature.

SUMMARY

An equation for predicting the thermal conductivity of pure organic liquids and its temperature coefficient has been derived and has been tested on a large number of liquids. Methods are given for predicting the variables involved where no data are available. 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. In the calculation of the intermolecular distance for chain compounds the assumption is made that the molecules are aligned, like rods in a bundle, perpendicular to the direction of heat flow. This arrangement is a good approximation for long-chain molecules. For shorter molecules the disorder increases and the molecular arrangement changes. The method is applicable also to other-shaped molecules. [For ring compounds *see* Part III (*16a*)] Although no data are given at this time, the intermolecular distance for ring compounds is calculated on the assumption that the rings are stacked like coins with their thickness perpendicular to the direction of heat flow. This arrangement is verified by X-ray–diffraction data of liquids and solids. For very small molecules, such as carbon tetrachloride, methyl chloride, and chloroform, the molecular volume is considered as a cube. In this case no X-ray–diffraction data are necessary.

ACKNOWLEDGMENT

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NOTATION

A = heat transfer area, normal to heat flow, sq.ft.
a = a constant
b = a constant
C_p = specific heat at constant pressure, B.t.u./ (lb.) (°F.)
d = mean intermolecular distance, center to center, ft.
d = molecular diameter, ft.
dt = temperature drop, °F.
k = thermal conductivity, B.t.u./ (hr.) (sq.ft.) (°F.)
L = mean intermolecular distance, surface to surface, ft.
l = molecular length, ft.
M = molecular weight, lb.
m = ratio of critical to minimum molecular volume
N = Avogadro's number, 2.73×10^{26} molecules/lb.mole
n = effective branching contribution
n = integer representing the order of diffraction
Q = thermal energy, B.t.u.
q = rate of heat flow, B.t.u./hr.
R = gas constant, 1.987B.t.u./ (lb. mole) (°R.)
R = additive constant
s = intermolecular distance, Å.
T = absolute temperature, °R.
t = temperature, °F.
t = molecular thickness, ring molecules only, ft.
U_s = velocity of sound, ft./sec.
V = molar volume at a given temperature, cu.ft./lb.mole
v = molecular volume at a given temperature, cu.ft./molecule
x = distance along X axis parallel to the direction of heat flow, ft.
x = sum of molecular diameter and mean intermolecular distance, $d + L$, ft.
x = thickness, ft.
y = distance along Y axis, parallel to the molecular length, perpendicular to the direction of heat flow, ft.
z = distance along Z axis, perpendicular to the molecular length, perpendicular to the direction of heat flow, ft.

Greek Letters

ρ = density, lb./cu.ft.
λ = wavelength of incident radiation, Å.
ϕ = scattering angle at maximum scattering intensity, degrees
ω = expansion factor

Subscripts

a = available
c = critical
f = freezing point
G = gas or vapor
L = liquid
0 = absolute zero
p = pressure
r = reduced

Conversion Factor

$1 \text{Å} = 3.28 \times 10^{-10}$ ft.

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APPENDIX

Calculation of Variables in Equation (8)

The use of Equation (8) requires reliable values of the variables involved. As few values of the velocity of sound in liquids have been published, it was necessary to survey the literature to develop a satisfactory method for predicting it where no values are available. The calculation of the available intermolecular distance requires X-ray–diffraction data. These data are available but require interpretation for use with Equation (8). Finally a satisfactory method for calculating the ratio of the critical to the minimum molecular volume had to be developed. In all instances it is important to note that the methods of evaluating the variables involved have a theoretical basis.

Specific heat. Reliable values of the specific heat of liquids are difficult to obtain. The most dependable values for a number of liquids have been collected by J. Timmermans (*20*). For other liquids the specific heat may be calculated from the specific heat of the ideal gas by the method proposed by Hougen and Watson (*7*). Chow and Bright (*2*) proposed an empirical method for predicting the specific heat of homologous series of liquids. A new method for calculating the specific heat of liquids at constant volume and at constant pressure has been developed by the authors and will be published later.

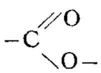
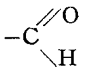
Density. Values of the liquid density at 68°F. are readily available. For values at other temperatures reference *20* may be consulted. Where no data are available, the method of generalized liquid densities proposed by Watson (*23*) is recommended.

Velocity of sound. Few values of the velocity of sound in liquids have been published in handbooks. However a literature survey was made by the authors (*16*), and data on a large number of liquids were collected and classified and a number of methods proposed by various investigators for predicting the velocity of sound in liquids are also given.

One of the simplest relations was proposed by Rao (*15*), who pointed out that

$$U_s = \left(\frac{R\rho}{M}\right)^3 \qquad (12)$$

TABLE 3.—STRUCTURAL CONTRIBUTIONS TO THE VELOCITY OF SOUND

Basic Radicals	R
CH_4	9.50
Benzene	23.25
Cyclohexane	27.50
Naphthalene	33.67
Additional Radicals or Atoms	
$-\overset{\vert}{\underset{\vert}{C}}-$, $-\overset{\vert}{C}H-$, $-CH_2-$, $-CH_3$	4.47
 $-C(=O)O-$	6.25
 $-CHO$	2.30
$-\underset{\underset{O}{\Vert}}{C}-$	4.47
$-NH-$	3.27
$-NH_2$	2.45
$-CO_2H$	4.83
$-C\vdots N$	4.20
$-O-$	1.40
$-OH$	0.70
$-Cl$	3.13
$-Br$	3.55
$-I$, $-NO_2$	4.58
$-S$, $=S$	2.82
Bonding	
$=$	−1.30
$\equiv$	−2.60
Position	
o—	0
m—	0.30
p—	0.60

He indicated that R is substantially independent of temperature and that it is an additive function of the molecular structure, as in the case of the parachor.

Calculations on a large number of liquids made by the authors indicated that the structural contributions to the velocity of sound as given by Rao had to be modified if the relation was to hold at all. As a result, modified structural contributions were proposed (*16*). Additional work has resulted in a different set of structural contributions to the velocity of sound (*see* Table 3) that appears to correlate the data more satisfactorily. Each compound is considered as composed of a basic group which is modified by the substitution of other groups for atoms comprising it. Hence all liquids having a chain structure are considered as derived from methane. Similarly any compound having a ring is considered as derived from benzene, cylohexane, or naphthalene as the case may be. The contributions of the four basic groups are given in Table 3. The method of calculation will be shown by an illustration.

ILLUSTRATION 1. Calculate the velocity of sound in *m*-chlorotoluene at 68°F.

Formula = $m\text{-}CH_3C_6H_4Cl$

Mol. wt. = 126.58

ρ = 66.75 lb./cu.ft.

Base group (benzene) ..		23.25
$—CH_3$	1 × 4.47	4.47
—Cl	1 × 3.13	3.13
m-position		0.30
	R =	31.15

$$U_s = \left(\frac{R\rho}{M}\right)^3 = \left(\frac{31.15 \times 66.75}{126.58}\right)^3 =$$

4,410 ft./sec

The value observed by Lagemann, McMillan, and Woolf (*9*) is 4,324 ft./sec.

The independence of the constant R with temperature will be shown for the case of *n*-heptane

Temp., °F.	$R_{obs.}$*
68	36.70
86	36.70
104	36.70
122	36.72
140	36.75

*Calculated from the data of Freyer, Hubbard, and Andrews (*5*).

The velocity of sound for 135 pure organic liquids of all chemical types was calculated by the authors, using the structural contributions given in Table 3, and it was found that the average deviation from the experimental values was ±2.6%. The maximum observed deviation was ±8.0%. Comparison of experimental values showed that the most reliable values may vary by about 1 to 2%, extreme values vary by about 6%. It must be noted that Equation (12) is applicable to both normal and associated liquids. A semiempirical equation for predicting the velocity of sound for normal liquids only has been proposed by Tsien (*21*).

Intermolecular distance. In order to calculate the available intermolecular distance L, the following variables must be known accurately: x, equal to $d + L$; v_c, critical volume; and v_c/v_0, ratio of critical to minimum molecular volume.

DIMENSION x. The dimension x is determined by X-ray–diffraction measurements. One method of analyzing the results is by using the simple Bragg's law

$$n\lambda = 2s \sin 1/2\phi \qquad (13)$$

The primary normal alcohols exhibit two scattering peaks. One of these has been identified as corresponding to the molecular length l and the other as the molecular diameter x, or distance from center to center of adjacent molecules. Thus for *n*-amyl alcohol $s_1 = 4.48$ Å.; $s_2 = 13.10$ Å.

The dimension s_1 corresponds to the molecular diameter x and is observed to remain constant from member to member of the series, as expected. The dimension s_2 corresponds to the molecular length and is observed to increase regularly as the number of carbon atoms increases. Actually the dimension s_2 represents two molecular lengths, where the alcohol molecules appear to be arranged in pairs head to head.

Strictly speaking, Bragg's law is applicable only when interference occurs over a large number of regularly spaced layers, as in a crystal. In the case of liquids the number of such layers that may be considered as regularly spaced is probably not large. In the extreme case of only two diffracting centers it has been shown(*3*) that the diffraction maxima occur at

$$\left(\frac{n+1}{n}\right)\lambda = 2s \sin 1/2\phi \qquad (14)$$

This differs from Bragg's law by the factor $(n+1)/n$ and indicates that for a real liquid the correct formula will be intermediate between Equations (13) and (14).

An alternative method, applicable strictly to liquids which consist of spherical molecules, has been developed by Zernicke and Prins (*24*) and Debye and Menke(*4*). This method consists of determining the radial distribution of molecules based upon the observed scattering intensity; however, unless the data have been obtained with high precision over a large range of s values, it may be questioned whether a more reliable value of the spacing is obtained by the radial distribution method than by Bragg's law(*3*). In any case the values found by the two methods differ by only a few per cent.

Since for the calculation of the thermal conductivity it is important to know the molecular diameter x, a survey of literature on scattering of X rays by liquids was made by the authors. The publishing data were recalculated on the basis of the equation

TABLE 4.—MOLECULAR DIAMETER x, Å., OF PURE ORGANIC LIQUIDS FROM X-RAY-DIFFRACTION MEASUREMENTS

at 68° F.

I. Straight-chain molecules

	C_1*	C_2	C_3	C_4	C_5	C_6† →
Acids	4.10	4.70	5.00	5.20	→	→
Alcohols	4.30	4.60	5.09	→	→	→
Aldehydes		4.45	5.01	5.20	→	→
Amides	4.13	4.80	5.10			
Amines (mono, di)			5.03	5.20	→	→
Esters			4.91	5.03	→	→
Ethers				5.29		
Halogenated hydrocarbons		4.70‡				
Hydrocarbons						5.40 →
Ketones			5.10	→	→	→
Mercaptans			4.96	5.01		
Nitrated alkanes		4.60**	5.01			
Nitriles		4.43	4.84			

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*The subscript indicates the number of carbon atoms in the molecule.
†The arrows indicate that the molecular diameter remains the same for all longer molecules.
‡Methyl iodide.
**Nitromethane.

II. Cyclic compounds (t dimension)*

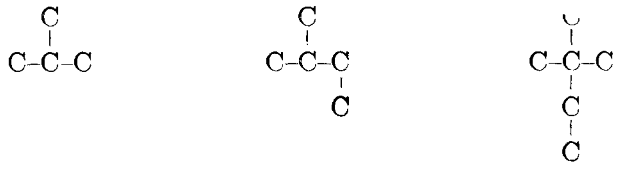
	t, Å
Benzene, pyridine	5.30
Naphthalene	5.81
Cyclopentane	5.50
Cyclohexane, piperidine	5.73
Cycloheptane	5.86

---

*The rings are presumed to have disk shapes and to be arranged in stacks. The t dimension refers to the thickness of the disk.

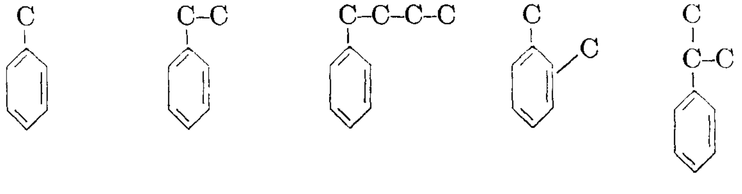
III. Branched contributions, straight-chain and cyclic compounds (Substitution of $—CH_3$ group for hydrogen $\Delta x = 0.42n$†)

1. Chain compounds*



$n = 1$ $n = 1$ $n = 2$

2. Cyclic compounds*‡



$n = 1$ $n = 1$ $n = 1$ $n = 2$ $n = 2$

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*The position of substitution is immaterial, 1- 2, 3, or 0, *m*-, *p*-, etc.
†The letter n refers to the number of substituent $—CH_3$ groups as shown in the illustrations. For example, if two $—CH_3$ groups are substituted in 2, 4- positions as in 2, 4-dimethyl pentane, the effective n is 1, since the molecule is presumed to be rotating, and the swept volume is the same whether one or two $—CH_3$ groups have been substituted. The same applies to the case of 2, 2, 4- dimethyl pentane.
‡The branched contribution should be added to the t dimension.

IV. Substitutions*

Substitution of hydrogen atom by	Δx, Å†	Δx, Å‡
1. NH_2, CHO	0.10	0.80
2. F, I	0.10	
3. OH	0	0.20
4. CN, O (ketone)	0	
5. NO_2	0.50	0.75

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*For ring compounds the contributions should be added to the t dimension.
†Single substitution. Substitution in combination with Cl, Br, the position of substitution is immaterial. Substitution in combination with —CHO, $—NH^2$ in *p*-position.
‡Substitution in *o*, and *m*-positions in combination with —CHO, $—NH_2$, —OH.

$$1.14\,\lambda = 2s \sin 1/2\phi \qquad (15)$$

which is intermediate between Equations (13) and (14) for $n = 1$.

Only the molecular diameter x was considered, since the remaining dimensions can be calculated from the geometry of the molecule and the liquid density. Actually many liquids, notably the hydrocarbons, show one diffraction peak only, corresponding to the x dimension.

It may be noted that these dimensions, determined from scattering data, can be used to calculate the liquid density on the basis of the proposed molecular arrangement. For alcohols

$$v = (s_2/2)\, s_1^2 \qquad (7c)$$

and from Equation (7*a*)

$$\rho = \frac{M}{Nv} = \frac{M}{N(s_2/2)s_1^2}$$

For *n*-amyl alcohol

$$\rho = \frac{88.15}{2.73\times10^{26}\ (6.55\times1.14\times3.28\times10^{-10})(4.48\times1.14\times3.28\times10^{-10})^2}$$

$$\rho = 47.0 \text{ lb./cu. ft.}$$

The observed liquid density at 68°F. is 50.7 lb./cu.ft.

The bulk of the literature data is summarized in Table. 4

The intermolecular distances determined from X-ray–diffraction measurements in pure liquids agree well with measurements on monomolecular liquid films and with studies on the structure of micelles formed in soap solutions. They approximate also values obtained from measurements on materials in the solid state. For example

	Liquid x, Å.	Solid x, Å.
Capric acid	5.21	4.79
Lauric acid	5.56	5.04
Palmitic acid	5.50	5.03
Erucic acid	5.45	5.09
Brassidic acid	5.55	5.06
Lauryl alcohol	5.25	4.79

If the effect of temperature is neglected, it will be noted that the dimension x increased on melting. Since for the solid both the x and l dimensions decrease as the temperature approaches absolute zero, it is possible that the length of the molecules as measured in the liquid state represents the minimum possible length. This would mean that the molecules on melting came together forming long chains, thus causing an increase in the dimension x as a result of the redistribution of the available volume.

The effect of temperature on the measured molecular dimensions has not been extensively investigated, but it is relatively small. The estimated accuracy of the values given in Table 4 is ±0.05 Å.

CRITICAL DENSITY, ρ_c. The critical density for a number of liquids is given in reference (*13*), and additional values may be found in *20*. For other liquids Watson's method of generalized liquid densities (*23*) is recommended.

RATIO OF CRITICAL TO MINIMUM MOLECULAR VOLUME, v_c/v_0. A number of empirical methods (*6, 10, 18, 19*) have been proposed for determining the molecular volume at absolute zero. The method presented here is based on the law of rectilinear diameter, according to which the arithmetical average of the densities of a pure unassociated liquid and its saturated vapor (orthobaric densities) is a linear function of the temperature. In equation form

$$\frac{1}{2}(\rho_L + \rho_G) = a - bT \qquad (16)$$

Although not exact, this relation is accurate for many substances and provides a very useful method for calculating the critical density, a quantity not readily measurable.

At absolute zero Equation (16) reduces to

$$\frac{1}{2}\rho_o = a \qquad (17)$$

At the freezing point the density of the vapor is very small and may be neglected, and so Equation (16) reduces to

$$\frac{1}{2}\rho_f = a - bT \qquad (18)$$

At the critical temperature the density of the vapor and liquid is the same and Equation (16) reduces to

$$\rho_c = a - bT_c \qquad (19)$$

Equations (17), (18), and (19) may be combined to eliminate the constants a and b. This results in

$$\rho_o/\rho_c = 2\left\{1 + \left(\frac{\rho_f/2 - \rho_c}{\rho_c}\right)\left(\frac{T_c}{T_c - T_f}\right)\right\} \qquad (20)$$

Equation (20) gives the ratio of the critical to minimum molecular volume v_c/v_0 from a knowledge of the critical density and temperature, density at freezing point, and freezing temperature.

In these calculations the freezing density was determined by Watson's relation (*23*)

$$\rho_f = \left(\frac{\rho_{68°\text{F.}}}{\omega_{68°\text{F.}}}\right)\omega_f \qquad (21)$$

The expansion factor was calculated by the equation (*23*)

$$\omega = 0.1745 - 0.0838\, T_r \qquad (22)$$

for $T_r < 0.65$. Values of the critical temperature will be found in the same tables giving the critical density. Other values for hydrocarbons may be estimated by the method of Michael and Thodos (*12*). Values for other liquids may be estimated by the method proposed by either Watson (*22*) or Meissner and Redding (*11*).

Equation (20) was found to be applicable for both normal and associated liquids. A few values will be given as an example:

Liquid	Method of Measurement	$v_c/v_{o\ obs.}$	$v_c/v_{o\ calc.}$ [Eq. (20)]
n-Pentane	Density*	3.80	3.82
Ethyl alcohol	Gas law	4.02	3.94
Ethyl alcohol	Compressibility†	4.10	3.94
Ethyl ether	Compressibility†	3.91	3.89

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*The lowest density measured was 47.9 lb./cu. ft. at 246°R. This value was extrapolated to 0°R.

†The volume at absolute zero may be regarded as given by the limiting volume of a liquid under infinite pressure, which can be calculated from the compressibility. In the case of liquids, at 68°F. and 11,600 atm. the reduction in volume is about 30%. Hence the density at 0°R. is obtained by ρ 68°F., 1 atm ÷ 0.70.

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