THE THERMAL CONDUCTIVITY OF LIQUIDS

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This note briefly summarizes new results on the thermal conductivity of liquids which will be described in greater detail in a forthcoming number of the *Proceedings of the American Academy of Arts and Sciences.* The results are of two kinds: in the first place measurements of the effect of pressure on thermal conductivity, and in the second place a theoretical expression for thermal conductivity.

The apparatus used in the measurements was a radial flow apparatus, in which the liquid was contained in the space between two concentric metal cylinders; the axis of the inner cylinder was a source of heat which flowed out radially across the layer of liquid. The temperature difference between the outer and inner surfaces of the layer of liquid was measured, and the thermal conductivity calculated in terms of the dimensions and the temperature difference. The method is particularly adapted to the measurement of substances of low conductivity like liquids, and gave results of much regularity and consistency. It is adapted to give not only the changes of conductivity under pressure, but also the absolute values of conductivity. The accuracy of the results is probably a few tenths of one per cent.

Fifteen liquids were measured in all. Many of these were the same as those for which I have previously determined the various thermodynamic properties under pressure.[1] The pressure range of this work was that usual to all my high pressure measurements, namely 12000 kg./cm.^{2}; the measurements were also made at two temperatures, 30° and 75°. Not only do the measurements give the pressure coefficient of conductivity, which has never been measured before for liquids, but also the temperature coefficient at atmospheric pressure, for which there are only a few discordant previous measurements, and the temperature coefficient of the pressure coefficient.

The new experimental results are contained in table I. The results for each liquid are given in two lines, in the first line are the results for 30° and in the second those for 75°. In the first column of figures are the values at atmospheric pressure of the absolute conductivity (in ordinary units, gm. cal. per cm.^{2} per sec. per degree C. per cm.), in the second column the ratio of the conductivity at 6000 kg. to that at atmospheric pressure, and in the third column the ratio of the conductivity at 12000 kg. to that at atmospheric pressure. The general results may be summarized as follows. At atmospheric pressure the conductivity decreases with rising

TABLE I

SUMMARY OF RESULTS ON THERMAL CONDUCTIVITY OF LIQUIDS

LIQUID	K, ABSOLUTE CONDUCTIVITY	$\frac{K_{6000}}{K_0}$	$\frac{K_{12000}}{K_0}$
Methyl Alcohol	0.000505	1.724	2.097
	493	1.785	2.191
Ethyl Alcohol	430	1.744	2.122
	416	1.845	2.278
Iso-propyl Alcohol	367	1.743	2.150
	363	1.890	2.211
N Butyl Alcohol	400	1.648	2.008
	391	1.720	2.099
Iso-amyl Alcohol	354	1.686	2.069
	348	1.724	2.126
Ether	329	2.009	2.451
	322	2.043	2.537
Acetone	429	1.659	Freezes
	403	1.738	2.137
Carbon Bisulfide	382	1.663	1.962
	362	1.789	2.154
Ethyl Bromide	286	1.657	1.928
	273	1.772	2.121
Ethyl Iodide	265	1.509	1.724
	261	1.570	1.837
Water	144	1.293	Freezes
	154	1.308	1.506
Toluol	364	1.604	Freezes
	339	1.738	2.089
Normal Pentane	322	1.987	2.481
	307	2.112	2.740
Petroleum Ether	312	1.970	2.379
	302	2.026	2.561
Kerosene	357	...	...
	333	1.654	2.054

temperature, except for water. At constant temperature the conductivity increases with rising pressure, the increase not being linear with the pressure, but the increase in the first 6000 kg. is relatively greater than in the second. The total increase under 12000 kg. varies from 1.5 to 2.7 fold, the increase being greater for the more compressible liquids. The proportional increase is greater at the higher temperature.

The second part of the paper has to do with a very simple theoretical picture in terms of which the conductivity may be calculated. It is surprising that practically no theoretical work has been done on the thermal conductivity of liquids. I know of no theoretical expression for the conductivity, and I have been able to find only one empirical expression, that of Weber.[2] It is known in a general way that the mechanism of conduction in a liquid is different from that in a solid or a gas. That the mechanism is different from that of a solid is shown by the fact that the conductivity is of a lower order of magnitude. That it is different from that of a gas is shown by the fact that the theoretical results for a gas do not hold. Thus the well known relation between thermal conductivity, viscosity, and specific heat of a gas breaks down entirely for a liquid. It has been shown, for example, that the viscosity of a dilute solution of glue in water may vary by a factor of many fold with very little change in the thermal conductivity.

In searching for a better understanding of the mechanism of thermal conduction in liquids, I have found the following expression for conductivity in terms of fundamental properties of the liquid:

$$K = 2\alpha v \delta^{-2}$$

Here k is the thermal conductivity measured in Abs. C.G.S. units, α is the gas constant 2.02×10^{-16}, v is the velocity of sound in the liquid, and δ is the mean distance of separation of the centers of the molecules, computed by assuming the molecules arranged in simple cubical array.

TABLE II

COMPARISON OF COMPUTED AND OBSERVED THERMAL CONDUCTIVITIES

LIQUID	VELOCITY OF SOUND	δ^{-2}	THERMAL CONDUCTIVITY COMPUTED	OBSERVED
Methyl Alcohol	1.13×10^5	6.00×10^{14}	27.4×10^3	21.1×10^3
Ethyl Alcohol	1.14	4.74	21.8	18.0
Propyl Alcohol*	1.24	3.94	19.7	15.4
Butyl Alcohol*	1.05	3.49	14.9	16.7
Iso-amyl Alcohol	1.24	3.13	15.7	14.8
Ether	.92	3.19	11.9	13.7
Acetone	1.14	4.00	18.5	17.9
Carbon Bisulfide	1.18	4.61	21.9	15.9
Ethyl Bromide	.90	3.97	14.5	12.0
Ethyl Iodide	.78	3.81	12.1	11.1
Water	1.50	10.4	63.0	60.1

* Calculations made for normal propyl and isobutyl alcohols, observed conductivities given for iso-propyl and normal butyl.

In table II are shown the values at 30° computed by the formula and determined by experiment for those liquids for which the necessary data are known. In making the computation, I have had to calculate the velocity of sound from my values of isothermal compressibility, making correction for the difference between isothermal and adiabatic compressibility, a difference which may rise to as much as 30 or 40%. There is probably some error in these values (my values for the thermodynamic constants at atmospheric pressure had to be determined by extrapolation), but in the absence of systematic measurements of the velocity of sound in liquids, it seems the best that we can do.

The formula may be deduced in terms of the following very simple physical picture. Let there be in the liquid a temperature gradient $d\theta/dx$. The energy of the molecule is $2\alpha\theta$ (half potential and half kinetic), where

θ is the absolute temperature. The difference of energy between neighboring molecules in the direction of the temperature gradient is $2\alpha\delta d\theta/dx$. This energy difference is to be conceived as handed down a row of molecules with the velocity of sound. The total energy transferred across a fixed point of any row of molecules per unit time is the product of the energy difference and the number of such energy steps contained in a row of molecules v cm. long, or $2\alpha\delta(d\theta/dx)(v/\delta)$. The total transfer across unit cross-section is the product of the transfer across a single row and the number of rows in unit cross-section, or $2\alpha v\delta^{-2}d\theta/dx$. But by the definition of thermal conductivity the transfer is also $kd\theta/dx$. Whence, identifying constants, we have for the thermal conductivity $2\alpha v\delta^{-2}$.

We see from table II that the agreement between theoretical and experimental values is much more than an agreement of order of magnitude, and is striking in view of the simplicity of the formula and the fact that this appears to be the first theoretical formula ever applied to the subject. It is interesting that the conductivity of water, which is three or four times as high as that of the ordinary organic liquid, is reproduced by the formula. The high conductivity of water appears, therefore, not to be due in any special way to the molecular peculiarities of water (two or more molecular species), but is directly referable to its low compressibility and the fact that the centers of the molecules in water are closer together than in the ordinary liquid.

The formula gives the right sign for the temperature coefficient of conductivity at atmospheric pressure, both for ordinary liquids and water. For the ordinary liquid, both v and δ^{-2} decrease with rising temperature, so that the conductivity would be expected to decrease with rising temperature, as it actually does, whereas for water v increases with rising temperature (both the isothermal compressibility and the thermal expansion of water vary abnormally with temperature) at a rate more than sufficient to compensate for the decrease of δ^{-2}, so that on the whole the conductivity should increase, as it does in fact.

The formula does not account well numerically for the effect of pressure. It of course gives the right sign for the pressure effect, for both v and δ^{-2} increase under pressure. But the increase of these two factors under pressure is such that an increase of conductivity under 12000 kg. of between three and four fold would be expected, whereas we have found that the actual increase is only 2.7 fold at the maximum. The reason for this failure is not far to seek. Our theoretical picture has represented the molecules of the liquid as standing in more or less coherent rows, so that the temperature energy may be handed from molecule to molecule down a row with little interference. It is not unnatural to suppose that the molecules tend to align themselves in this way when the intermolecular forces are allowed free play, for it is known that in the surface films of many liquids the molecules do form into rows. But when external compulsion is applied, as by the application of external pressure, the molecules are no longer able to take their natural arrangement, but are forced into less natural positions, the coherent rows are broken up, the transfer of energy is interfered with, and the thermal conductivity is therefore less than to be expected according to the simple picture. This agrees with the observed fact that the increase of conductivity under pressure is less than that given by the simple formula.

Further refinement of the picture would obviously demand a detailed knowledge of molecular structure and of the fields of force surrounding the molecules.

[1] Bridgman, P. W., *Proc. Amer. Acad., Boston,* **49,** 1913 (1–114).

[2] Weber, H. F., *Sitzber. Ber. Akad., Berlin,* 1885^2 (809–815).

PHOTOVISUAL MAGNITUDES OF ONE HUNDRED BRIGHT STARS

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The combined results of my extra-focal observations for the photographic magnitudes of the brighter stars are given in *Harvard Annals,* **76,** No. 6. According to this system, the photographic magnitudes were made to correspond to Professor Pickering's photometric magnitudes for stars of Class A0.

The color indices, derived by subtracting the photometric from the photographic magnitudes, are in good agreement with the results of Parkhurst[1] and Schwarzschild.[2] Parkhurst used a Zeiss doublet lens of ultraviolet glass; Schwarzschild used a Zeiss Tessar lens; while I employed three different instruments, namely, the 11-inch Draper, the 13-inch Boyden, and the 8-inch Draper telescopes. Parkhurst placed his plates 0.6 cm. inside of focus; Schwarzschild placed his plates from 0.05 to 0.10 cm. inside of focus. All of my plates have been 1.25 cm. or more outside of focus. The accordance of the several results is probably due to the fact that extra-focal images partake but little of the idiosyncrasies of the individual telescope. Herein they have great advantage over focal images. Moreover, all the instruments were refractors. I have shown elsewhere that color indices found with the 24-inch Harvard Reflector[3] are less than those obtained with the 8-inch Draper telescope. This is due to the selective reflectivity of a silvered surface.

The present investigation concerns the *photovisual* magnitudes of bright