

Thermal Conductivity of Water at High Pressures

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The thermal conductivity of water has been measured between 30° and 140°C at pressures ranging up to 8000 kg/cm² using Bridgman's concentric cylinder technique. At atmospheric pressure, the values obtained are about 1% less than the most probable values estimated by Powell. At higher pressures, the values agree well with Bridgman's measurements where the data overlap. The results are discussed in terms of Hall's two fluid model of water.

INTRODUCTION

OF the many investigations on the thermal conductivity of water, recently reviewed by Powell,¹ only two pertain to experiments carried out under high hydrostatic pressures, those of Bridgman² and of Timrot and Vargaftik.³ The latter, whose data extend only to 400 kg/cm², found a pressure coefficient about 30% higher than the former, whose data extend to 12 000 kg/cm². This note contains data on the thermal conductivity of water in the temperature range from 30° to 140°C at pressures up to 8000 kg/cm², the limits of both variables being determined by design factors discussed below.

The properties of water are of considerable theoretical as well as practical interest owing to the many anomalies in its behavior.⁴⁻⁶ The thermal conductivity is no exception. Although in most liquids it decreases with increasing temperature, in water it increases near room temperature, passing through a maximum near 130°C. The cause of this behavior is not known but may be associated with the collapse of ice-like molecules in the water at higher temperatures. It is hoped that the more extensive data as a function of pressure presented here will be helpful in clarifying this phenomenon.

EXPERIMENTAL TECHNIQUE

All our measurements were made with an apparatus involving radial flow between closely spaced concentric cylinders. The conductivity cell which is patterned after that used by Bridgman² is shown in Fig. 1. This type of cell is uniquely suited for high-pressure studies because of its compact construction and the relatively small end corrections which are much more important in a cell surrounded by a pressure transmitting medium than they are in a cell surrounded by air. Several modifications have been made in Bridgman's design to facilitate obtaining accurate

data for water which becomes highly corrosive at high temperatures and pressures. These modifications are: (1) an extra inlet to the cell to permit rapid and thorough cleansing; (2) a staggered set of slotted rings which ensure good thermal contact with the inner wall of the pressure chamber without impeding the rapid transmission of pressure changes; (3) the use of pure silver to reduce the formation of insulating films on the inner surfaces of the cell.

The details of the final design are shown in Fig. 1. The cylindrical layer of water *A* is enclosed between two concentric silver cylinders, *B* and *C*, whose radial spacing (approximately 0.040 cm) is maintained by 2-mil nickel rings at the ends. The details of the end construction, including the nickel rings, is shown in Fig. 2. Heat is produced at the center of the assembly by an 0.005-in. Nichrome wire mounted in a glass capillary which electrically insulates it from cylinder *C*. Thermal contact is made with the pressure bomb by alternate split brass expansion and contraction rings *F*. Half of the rings open out against the bomb; the remainder close in against *B*. A spring *G* maintains thermal contact between the alternate rings. This arrangement provides good thermal path for the flow of heat from the conductivity cell but permits rapid mounting of the cell in the bomb.

Heater current is supplied to the Nichrome resistance by an external storage battery. This current, as well as the potential drop across the heater, was measured with a Leeds and Northrup K-2 potentiometer.

The average drop in temperature across the water, normally less than 1°C, was measured by three thermocouples *E*, connected in series and inserted in 0.013-in. holes drilled lengthwise through *B* and *C* at 120° intervals. The thermocouples were made of copper and constantan, butt silver-soldered and insulated with six baked coats of Corex varnish. These couples were calibrated by direct comparison with a platinum-platinum 10% rhodium thermocouple certified by the National Bureau of Standards.

Two openings in the cell, *H* and *J*, facilitate flushing and filling the cell. During filling, *J* is closed with a screw-on cap. Bellows *K*, consisting of a thin-walled tin tube mounted on a brass stem, are screwed into aperture *H*. The tube, initially open at the top is filled

¹ R. W. Powell, *Advances in Phys.* **7**, 276 (1958).

² P. W. Bridgman, *Proc. Am. Acad. Arts. Sci.* **59**, 141 (1923).

³ D. L. Timrot and N. B. Vargaftik, *Zhur. Tekh. Fiz.* **13**, 1063 (1940). A translation may be purchased from Associated Technical Services, Inc., P. O. Box 271, East Orange, New Jersey.

⁴ L. Hall, *Phys. Rev.* **73**, 775 (1948).

⁵ A. H. Smith and A. W. Lawson, *J. Chem. Phys.* **22**, 351 (1954).

⁶ T. A. Litovitz and E. H. Carnevale, *J. Appl. Phys.* **26**, 816 (1955).

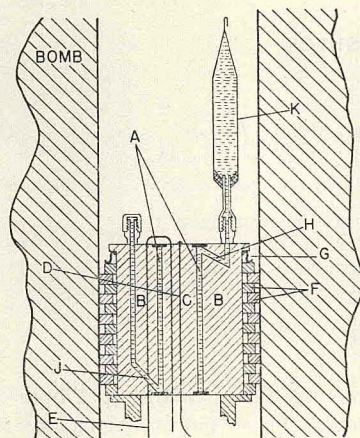


FIG. 1. Thermal conductivity cell. *A*, thin annulus containing sample; *B*, outer silver cylinder; *C*, inner silver cylinder; *D*, Nichrome heater contained in glass capillary; *E*, thermocouple; *F*, split, staggered spacing rings; *G*, spring; *H*, inlet tube; *J*, outlet tube; *K*, storage bellows.

with several cubic centimeters of distilled water. The whole cell is then placed in an evacuated bell jar to force the water into the annular space between *B* and *C*. This process is repeated several times until the cell is full. The bellows are then sealed at the top by folding it over tightly like the bottom of a toothpaste tube.

Pressure was transmitted to the cell by silicone oil filling the bomb and was measured by a manganin resistance gauge except for the lowest pressure run at 8 kg/cm^2 for which a bronze tube gauge was used. A constant sink temperature was maintained by an oil bath surrounding the bomb.

RESULTS

In the crudest approximation, the heat conductivity of the water is found by dividing the total power input in the heater by the steady state difference in temperature between the inner and outer junctions of the thermocouples. A more accurate determination is made by making a number of small corrections.

Four corrections are required to account for the heat which flows to the sink without passing through the thin annulus of water. Some heat escapes directly from the resistance wire and cylinder *C*, through the silicone oil, to the pressure vessel. By varying the height of the silicone oil above the cell at atmospheric pressure, this

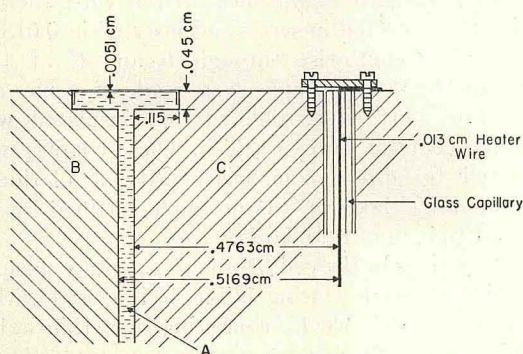


FIG. 2. Details of conductivity cell construction.

leakage was found to be negligible ($=0.1\%$). Some heat leaks through the silicone oil from the inner cylinder *C* to the outer cylinder *B*. By changing the amount of silicone oil around the cell, this leakage was found to be 0.6% at atmospheric pressure. Following Bridgman, we assume this leakage is entirely due to conduction and scale the correction as a function of temperature and pressure proportionately to the conductivity. This procedure requires a knowledge of the conductivity of DC-200 silicone oil at several temperatures and pressures. Because this information was lacking, rough determinations of this quantity were made. The results are shown in Fig. 3, where they are compared with the sparser data previously obtained by Bates.⁷ The change in slope of the temperature dependence with pressure is the usual behavior observed by Bridgman² for hydrocarbons, the reversal taking place in the same pressure range.

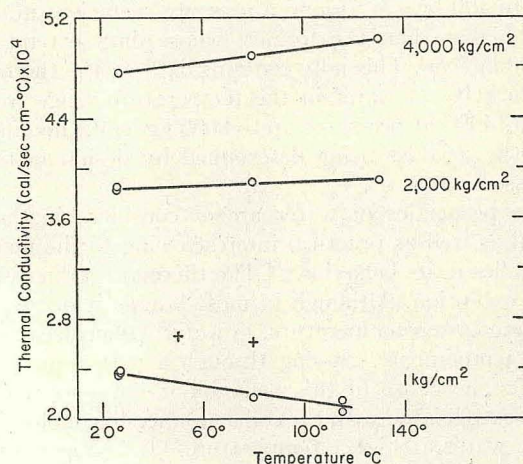


FIG. 3. Thermal conductivity of silicone oil (Dow Corning 200, 3 centistoke) as a function of temperature and pressure. The crosses are the previous values determined by Bates.⁷

Some heat flows through the widened section of the cylindrical annulus. This correction is purely geometrical. Since the total correction is only about 0.5% , it was made neglecting fringing effects.

By far the biggest correction is for the heat flow through the nickel rings which may amount to 5% . This correction is made by using a value of $k_{Ni} = 0.145 \text{ cal/}^\circ\text{C-cm-sec}$ at room temperature and pressure and scaling the correction in proportion to the known variation of the electrical conductivity.⁸ This correction may be in error by as much as 10% , primarily because of the uncertainty in the thickness of the rings.

Finally, a correction must be made for the drop in temperature occurring in the silver cylinders, *B* and *C*, owing to the finite distance between the thermocouple junctions and the walls. This correction which amounts

⁷ O. K. Bates, *Ind. Eng. Chem.* **41**, 1966 (1949).

⁸ A. W. Lawson, *Progr. in Metal Phys.* **6**, 1 (1956).

TABLE I. Thermal conductivity of water in units of 10^{-5} cal/cm-sec- $^{\circ}$ C. Add 2 to each value to obtain adjusted values in agreement with most probable values at 1 kg/cm 2 .

P/T	30 $^{\circ}$ C	50 $^{\circ}$ C	70 $^{\circ}$ C	90 $^{\circ}$ C	110 $^{\circ}$ C	130 $^{\circ}$ C
1 kg/cm 2	146	152	156	159	162	...
1000	155	162	167	172	175	178
2500	169	176	182	187	191	195
4000	180	188	194	199	205	210
6000	193	201	207	213	218	223
8000	204	212	220	226	231	236

to 1.1% at room temperature scales with the conductivity of the water.

The values obtained, after all the corrections mentioned above have been made, are shown in Table I.

Our values are systematically about 1% lower than the most probable values suggested by Powell¹ on the basis of a detailed analysis of all previous data. The two sets of values for one atmosphere are compared in Table II. The origin of this systematic difference is unknown. We have neglected heat transmission by radiation or convection which tends to make our results too high. We are inclined to believe that the discrepancy is associated either with a lack of concentricity of the cylinders *B* and *C* or with a small temperature gradient along the axis of the heater. Since we are mainly concerned with the pressure variation of the thermal conductivity, no special efforts were made to eliminate these sources of error. Bridgman estimates that radiation effects introduce an error no greater than about 1%, and presumably much smaller. According to an analysis carried out by Timrot and Vargaftik, convection effects should be negligible for our experimental conditions.

The only previous determinations of the heat conductivity of water as a function of pressure are those of Bridgman² to 12 000 kg/cm 2 at 30 $^{\circ}$ and 75 $^{\circ}$ and those of Timrot and Vargaftik³ to 400 kg/cm 2 from room temperature through the critical temperature. The increase reported by the former is $6 \times 10^{-3}\%$ per atmosphere while the latter found an increase $8 \times 10^{-3}\%$ under the same conditions. The corresponding value computed from Table I is $6.5 \times 10^{-3}\%$. Actually, as Riedel⁹ has pointed out, all Bridgman's values for

TABLE II. Comparison of atmospheric pressure data in units of 10^{-5} cal/cm-sec- $^{\circ}$ C with most probable values of Powell.^a

	30 $^{\circ}$ C	40 $^{\circ}$ C	50 $^{\circ}$ C	60 $^{\circ}$ C	70 $^{\circ}$ C	80 $^{\circ}$ C
Authors	146	149	152	154	156	158
Most probable	147	150	153	156	158	160
Difference	0.7%	0.7%	0.8%	1.1%	1.2%	1.0%

^a See reference 1.

⁹ L. Riedel, Chem.-Ingr.-Tech. 23, 321 (1951).

TABLE III. Bridgman's corrected data in units of 10^{-5} cal/cm-sec- $^{\circ}$ C. (Subtract 1% to obtain adjusted values in agreement with most probable data at one atmosphere.)

P/T	30 $^{\circ}$ C	75 $^{\circ}$ C
1 kg/cm 2	148+	159
1000	157+	170
2000	165+	179
4000	180+	196
6000	193+	210

thermal conductivity involve an average correction for end effects and consequently may be appreciably in error. We have corrected Bridgman's results for water and these results are shown in Table III. The corrected results are about 3% higher at atmospheric pressure than those reported by Bridgman and about 1% higher than the most probable values suggested by Powell. If we adjust both Bridgman's values and our values to agree at atmospheric pressure with the most probable values and introduce the same percentage correction at all higher pressures, the curves shown in Fig. 4 are obtained. The agreement with Bridgman at low pressures is very good but our values at higher pressures become progressively larger.

DISCUSSION

The behavior of the thermal conductivity of silicone oil reported above is typical of the behavior of normal fluids. At atmospheric pressure, the thermal conductivity decreases with increasing temperature; at higher pressures, it increases. For most hydrocarbons,

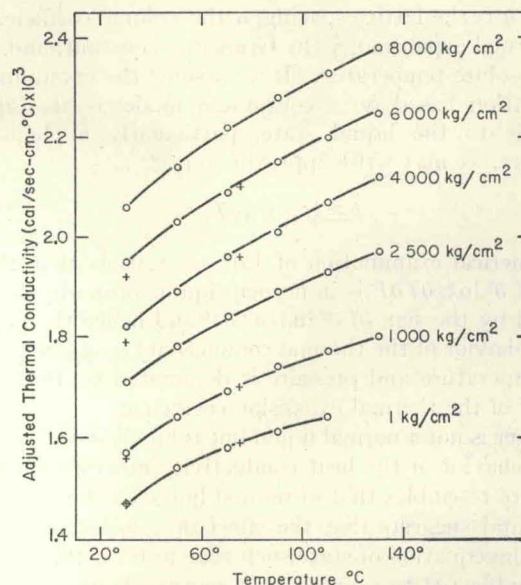


FIG. 4. The thermal conductivity of water as a function of temperature and pressure. These data have been adjusted to agree with the most probable values at atmospheric pressure. The crosses are Bridgman's data similarly adjusted.

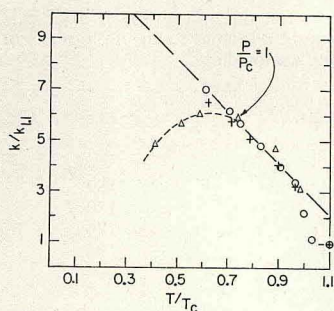


FIG. 5. The thermal conductivity of A, N₂, and H₂O as a function of reduced temperature. The ordinates are the ratio of the conductivity k to its value at 1.1 times the critical temperature T_c . The circles represent data on argon [A. Uhler, Jr., *J. Chem. Phys.* **20**, 463 (1952)]; the crosses, data on nitrogen (see Uhler); the triangles, water.

the pressure at which the temperature derivative of the heat conductivity undergoes a reversal in sign is about 3000 kc/cm². Bridgman¹⁰ has called attention to the fact that a similar reversal in sign occurs in the temperature derivative of the thermal expansion coefficient at about the same pressure. We believe that there is a direct connection between these two phenomena. The heat conductivity arises from the transport of energy by phonons and is ultimately limited by the scattering of these phonons in the medium. From kinetic theory, we may write for the heat conductivity k

$$k \cong \frac{1}{3} c_v \cdot v \cdot \lambda, \quad (1)$$

where c_v is the specific heat per unit volume, v the velocity of sound, and λ the mean free path. In a homogeneous insulating medium, the only available scattering mechanism is phonon-phonon scattering. In the case of a solid at high temperatures, this effect has been treated phenomenologically and an expression for the λ has been derived,¹¹ namely

$$\lambda \cong a / \alpha \gamma T, \quad (2)$$

where a is the lattice spacing, α the volume coefficient of thermal expansion, γ the Gruneisen constant, and T the absolute temperature. If we assume the crystalline calculation based on a continuum model is also applicable to the liquid state, particularly at higher pressure, we may write approximately

$$k \cong \frac{1}{3} c_v v a / \alpha \gamma T. \quad (3)$$

A numerical examination of Eq. (3) reveals that the sign of $\partial^2 \ln k / \partial T \partial P$ is in normal liquids primarily controlled by the sign of $\partial^2 \ln \alpha / \partial T \partial P$ and hence the normal behavior of the thermal conductivity as a function of temperature and pressure is dominated by the behavior of the thermal expansion coefficient.

Water is not a normal liquid but is highly associated. The behavior of the heat conductivity at atmospheric pressure resembles that of normal liquids at high pressures and suggests that the effect of association is to alter the equation of state such that water acts as if it were subjected to a pressure of several thousand bars

under ordinary atmospheric conditions. However, the thermal expansion coefficient in the range of temperatures above 40°C is normal, the reversal in the sign of $\partial^2 \ln \alpha / \partial T \partial P$ occurring at about 6000 bars. It is difficult, therefore, to ascribe the anomalous behavior of the thermal conductivity of water to an effect of this sort.

The increase in conductivity in water with increasing temperature might alternatively be due to the transport of excitation energy by diffusing molecular groups. Gierer and Wirtz¹² have measured the excess mobility of H⁺ and OH⁻ ions in water. They suggest that this excess mobility is an activated process associated with broken hydrogen bonds in dimers and quadimers of H₂O. In a temperature gradient such ions would diffuse and carry with them the activation energy required for their formation. It is perhaps significant that the excess mobility rises and passes through a maximum at about the temperature at which the heat conductivity is a maximum as a result of the shifting distribution of n -mers in the water. It would be interesting to investigate this excess mobility as a function of pressure. Such diffusing ions would contribute to the thermal conductivity of water and would be expected to increase its value above the value normally expected for liquids. If the "normal" behavior for the heat conductivity of water were known, it would be possible to decide if such an anomalously high conductivity exists at high temperature. Using the concept introduced by Riedel⁹ of a generalized formula for the reduced heat conductivity of normal liquids as a function of reduced temperature, we have estimated the "normal" behavior for water. In Fig. 5 we have plotted the ratio of the thermal conductivity at any temperature T to that at $T = 1.1 T_c$ as a function of T/T_c , where T_c is the critical temperature, for A, N₂, and H₂O. At high temperatures, the curves coalesce, indicating that above 100°C the behavior of water becomes normal in the sense that there appears to be no extra contribution to the heat conductivity. On the contrary, the heat conductivity for water appears to drop progressively below the expected value for normal liquids as the temperature is decreased.

TABLE IV. Estimated values of ΔF , ΔH , ΔS , and x_1 .

	ΔF (0°C)	ΔF (30°C)	ΔS	ΔH	x_1 (0°C)
	cal/mole	cal/mole	cal/mole-°C	cal/mole	
Authors	-150	-500	11.5	3000	0.42
Hall ^a	+500	(+500)	0.70
Litovitz and Carnavale ^b	-500	-650	5	870	0.30
Smith and Lawson ^c	0	-285	9.5	2600	0.50

^a See reference 4.

^b See reference 6.

^c See reference 5.

¹⁰ P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, London, 1938).

¹¹ A. W. Lawson, *Intern. J. Phys. Chem. Solids* **3**, 155 (1957).

¹² A. Gierer and K. Wirtz, *J. Chem. Phys.* **17**, 745 (1949).

The anomalously low values of k at low temperatures suggest that some other mechanism than thermal agitation is limiting the mean free path. This clue is reminiscent of Eucken's¹³ model of water as consisting of a number of polymers. This model has been simplified by Hall,⁴ who regards the water as existing in two states differing in free energy by ΔF cal/moles and in molal volume by ΔV cc/mole. Using this model, Hall attempted to explain the excess absorption of sound observed in water. His model was subsequently used by Smith and Lawson⁵ to discuss the temperature and pressure dependence of the velocity of sound and in slightly modified form by Litovitz and Carnevale⁶ to explain the pressure dependence of sound absorption.

Briefly, the theory treats water as a mixture of two types of molecules, whose mole fractions x_1 and $1-x_1$ are related by the equation

$$x_1/(1-x_1) = e^{-\Delta F/RT}. \quad (4)$$

If we treat one type of molecule as a foreign impurity, then the mean free path of phonons will be limited by impurity scattering as well as by thermal scattering. The resultant mean free path will be given by

$$1/\lambda = 1/\lambda_i + 1/\lambda_t, \quad (5)$$

where λ_i is the mean free path in the absence of thermal scattering and λ_t is the mean free path in the absence of impurity scattering. Since, as we know from simple kinetic theory, λ_i is proportional to x_1^{-1} , the difference between the reciprocal of the heat conductivity of water and that for normal fluids should depend on x_1 . If we assume c_v and v are independent of temperature (approximately true for water but not necessarily for normal liquids), the difference between the reciprocals should be proportional to x_1 , or, for small x_1 , should vary with temperature as $\exp(-\Delta H/RT)$, where ΔH is the heat of activation of the excited state of water. With-

¹³ A. Eucken, *Nachr. Ges. Wiss. Göttingen* **1**, 36 (1946); *Z. Elektrochem.* **52**, 255 (1948); *Z. Elektrochem.* **53**, 102 (1949).

in experimental error, this temperature dependence is observed for the difference in the reciprocals of the two curves of Fig. 5. By calculating the difference at these temperatures, it is possible to evaluate ΔF in Eq. (4), or more explicitly, ΔH and ΔS for the activated state, and hence to find x_1 as a function of temperature. We have carried out this calculation based on a reasonable curve through the points in Fig. 5 representing the behavior of normal liquids. The results of this calculation are shown in Table IV where the values of x_1 , ΔS , ΔH , etc., are compared with estimates made by previous investigators. All the estimates of ΔH , ΔS , etc., are based on the form of Eq. (4). If the statistical mechanics of a more precise model leads to a somewhat different form, e.g., $x_1^2/(1-x_1) = e^{-\Delta F/RT}$, the values for ΔF , etc. would be different but the consistency would be comparable. The values of x_1 are only slightly dependent on the form of Eq. (4). It is perhaps noteworthy that Gierer and Wirtz found activation energies of 2400 cal/mole and 3000 cal/mole for the excess mobilities of H^+ and OH^- ions, respectively, i.e., near the range of values for the energy of hydrogen bonds. The agreement of the values of ΔH and x_1 obtained from thermal conductivity data with sound velocity and absorption data is quite satisfactory in view of the approximations involved and lends credence to Hall's two fluid model. We remark that a value of x_1 which measures the preponderance of the "ice-like" state in excess of 50% would require a minimum in k , which is not observed. For this reason, we believe that the heat conductivity favors the modification of Hall's theory suggested by Litovitz and Carnevale. This modification is consistent with the analysis of Smith and Lawson.

ACKNOWLEDGMENTS

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