of the helium flow rate over a factor of about three produced scarcely any change in the chromatograph peak height of the biphenyl, whereas according to both mechanisms, a change should have been seen. In retrospect, it is unfortunate that we provided no means to directly measure the temperature of the vaporizing biphenyl itself, but relied on measurement of the thermostat temperature.

The present work, though preliminary in character, indicates that the chromatographic method should be capable of providing accurate vapor-pressure data if thermal and vaporization equilibria are achieved, as suggested by the result for liquid biphenyl at 354.2K. Careful application of the method may offer a way to fill in the gap that exists at present both for the liquid and the solid at temperatures close to the melting point.

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Thermal Conductivity of Distilled Water as Function of Pressure and Temperature

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Results of the experimental observations of the thermal conductivity of distilled water for the pressure range of atmospheric to 1400 bars and temperatures from 0° to 30°C are presented. Data are obtained with a concentric cylinder apparatus and have an estimated accuracy of about ±1%. These data are compared with those previously reported in the literature and the differences noted.

The thermal conductivity of pure water is an important property, especially in studies of heat transfer and molecular diffusion. It is also interesting because of its maximum, at saturation pressure, near 130°C (*7, 8*). Although the number of investigations of the thermal conductivity of pure water at atmospheric pressure are many (*5*), the thermal conductivity of pure water at elevated pressures has only been studied by a limited number of investigators (*1, 3, 8*). The results reported here are intended to supplement existing data and to present new data in the high-pressure, low-temperature region.

Experimental

The thermal conductivity of distilled water was measured by a concentric cylinder apparatus of the type used by Bridgman (*1*) and Lawson et al. (*3*) but was modified to minimize errors produced by heat loss. The cell (Figure 1) consisted of concentric silver cylinders (A_1 and A_2) sealed with O-Rings (B) and concentrically maintained with polycarbonate plastic rings (C). Both the rings and cylinders were scribed after precise measurement to determine the optimal (most concentric) orientation to allow for reproducible assembly. The resultant deviation from concentricity was 0.0025 cm or 5.0% of the liquid film thickness. The total length of the cylinders between the O-rings was 6.9126 cm which was approximately 130 times the film thickness of 0.0513 cm. The thin-film thickness was chosen to minimize possible interferences from convective currents.

The ends of the cylinders were thermally insulated from the surroundings by a pair of 0.635-cm thick General Electric 11617 laminated plastic end caps (D) which were attached by nylon screws (E). There was a central hole (F) through the end caps which served as an entry for the heating element and was sealed with self-curing silicone rubber after cell assembly, thus minimizing heat loss to the pressurization fluid. Thermocouple entry was provided by holes (G) in the end caps. The cell was maintained in good thermal contact with the pressure vessel by a staggered set of split copper rings (H). The fluid under investigation was located between the cylinders and isolated from the pressurizing fluid by a flexible thin latex bulb (J) which acted as a pressure compensator.

Heat flow (Q) by conduction through a circular cylinder, which is homogeneous and long enough to neglect end effects, is given by:

$$Q = -2\pi K L r \frac{dt}{dr} \tag{1}$$

where K is the thermal conductivity, r is the radius, L is the length of the cylinder, and dt/dr is the radial temperature gradient. Separating variables and integrating with boundary conditions of t_0 at r_0 and t at r yields:

$$t - t_0 = \frac{Q}{2\pi K L} \ln \frac{r_0}{r} \tag{2}$$

Rearranging Equation 2 gives

$$K = \frac{Q}{2\pi L(t - t_0)} \ln \frac{r_0}{r} \tag{3}$$

In Equation 3, ln $(r_0/r)/2\pi L$ is a geometrical constant, C, peculiar to the experimental cell, and Q, the heat input rate in watts, and $(t - t_0)$, the temperature differential across the annulus, are the experimental variables. The geometrical constant C for this experiment was $-1.4163 \pm 0.0025 \times 10^{-3}$ cm^{-1} where $r_0 = 0.80716$ cm, $r = 0.85837$ cm, and $L = 6.9126$ cm.

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In all the experiments, heat was generated with a No. 36 Nichrome V resistance wire which measured between 8.51–8.64 cm in length with a 2.5-cm length of No. 32 constantan welded to each end, which, in turn, terminated in a quartet of copper leads, two welded to each end. The entire assembly was electrically insulated with thin wall tetrafluoroethylene tubing and inserted as a loop through a small hole drilled in the axis of the inner cylinder (F of Figure 1).

Power was supplied with a Hewlett-Packard 6291A dc regulated power supply, and the input current was measured from the voltage drop across a calibrated Leeds and Northrup standard 1-ohm resistor (Figure 2). The resistance of the heating wire was determined from the voltage drop across the remaining pair of leads, thus allowing an accurate determination of the heat generated. Both of the potentials above were measured with a calibrated Hewlett-Packard Model 3440A digital voltmeter with a Model 3443A high gain amplifier (Figure 2).

The temperature differential generated across the two cylinders was measured with six matched and calibrated 0.159-cm diameter Conax metal-sheathed thermocouples. These thermocouple probes were arranged symmetrically, three on the interior cylinder and three directly opposite on the exterior cylinder (G of Figure 1). Two different sets of thermocouple junctions were used, one of iron–constantan and the other chromel–constantan. In each instance, the junction was situated as close to the wall as possible. Opposing couples were connected to generate a voltage proportional to the temperature differential, and the three EMF's generated were summed electrically and conducted to the exterior of the pressure vessel. This emf was then measured with a Leeds and Northrup Model K-3 potentiometer, calibration traceable to the National Bureau of Standards (Figure 2).

Other associated instrumentation used in this experiment (Figure 2) include a pressure-generating and measuring system consisting of a hand pump for rough pressure adjustment and a screw pump for fine pressure adjustment, a pair of calibrated temperature compensated Heise gages of 0–700 and 0–1400 bar ranges, a Hewlett-Packard Model 2801A quartz crystal temperature measuring system, and an Aminco temperature controlling and circulating water bath.

Procedure

The cleaned parts of the cell were rinsed twice with distilled water and then submerged in a small clean container of the same fluid. The assembly was accomplished while totally submerged to eliminate air bubbles, taking care to ensure that all scribe marks were aligned. Following assembly, the cell was removed from the tank and the exterior dried. The insulated heating element was then inserted and secured by wrapping the wire around two of the nylon screws.

The clearance remaining between the heating element and the central hole in the insulating end cap was plugged with Dow Corning 731 RTV silicone rubber and cured for 2 hr. After cure, the thermocouples were positioned in the cell, and the total assembly was inserted in the pressure vessel. The various electrical leads were made by soldering to pins of the high-pressure feedthroughs. The pressure vessel was completely filled with 3M FC-77 fluid, the ends were capped, the pressure line was attached, and the vessel placed on its side on a stand in the temperature bath.

Initially, the vessel was pressurized to approximate the desired level, the power supply turned on, and 15 min allowed for equilibration. At this time, the pressure was adjusted with the hand screw pump to the precise value desired, and the temperature differential monitored by the thermocouples. When the thermocouple emf reached a constant value, heater current, voltage drop, thermocouple emf, pressure, and bath temperature were measured and recorded. The pressure was then changed, and the cycle repeated for all values of pressure at that particular temperature.

After all values were measured, the temperature was raised 10°C, and the whole cycle was repeated. When measurements at all temperature and pressure points were completed, the pressure vessel was opened, and the thermocouple set was replaced by one of different junctions and the series repeated.

Thermal conductivity was measured at eight pressures and at four chosen temperatures (0°, 10°, 20°, and 30°C). The pressure sequence at any temperature was a loop of 10, 200, 600, 1000, 1400, 1200, 800, and 400 bars, and finally a repeat at 10. No measurements of thermal conductivity were undertaken at 1-atm pressure because the pressurization fluid, FC-77, was observed to boil, leading to erratic results.

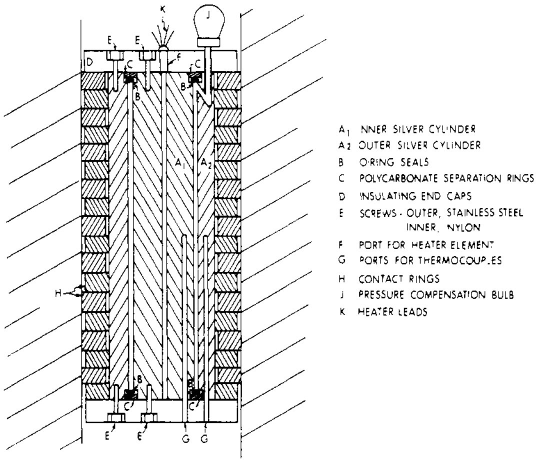

Figure 1. High-pressure thermal conductivity cell in pressure vessel

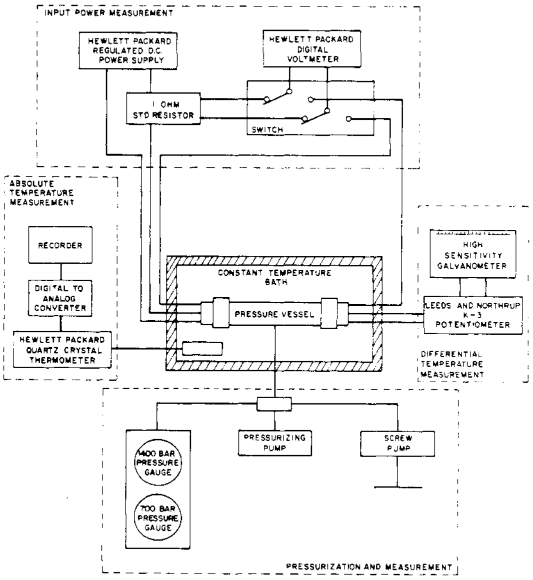

Figure 2. Experimental setup

Accuracy and Error

Two distinct series of measurements were conducted utilizing different thermocouple junctions. Each series consisted of at least three determinations of each data point and many determinations of selected "reference" data points, primarily at 10 and 25 bars pressure. In almost all cases, the data resultant from any particular series agrees to within 0.2% of the mean value. This small variation was traced to the procedure used to measure the temperature differential.

The setup required solder joints to mate the thermocouple leads to the high-pressure electrical feedthroughs. These joints required unsoldering and resoldering during each assembly of the apparatus. This caused a variation in the thermocouple emf of 0.5 μV, which is ±0.2% of the approximately 130–150 μV generated by the temperature gradient.

The accuracy of thermocouple differential temperature measurement can only be estimated and is thought to be ±0.5%, based upon comparison of the results obtained with both sets of thermocouples. This estimate is believed to be conservative because of the small temperature differential (1.0°C) between the cylinders. The emf values used to calibrate the thermocouples and generate the least-squares 10th degree interpolation polynomial were obtained from the National Bureau of Standards (*4*).

The temperature bath around the pressure vessel was controlled to ±0.01°C, and its temperature measured with a quartz crystal thermometer with absolute accuracy (after ice point calibration) of ±0.05°C. An error of ±0.05°C in this measurement results in an inaccuracy of ±0.02% in *K*, the thermal conductivity.

The pressure was measured with Heise pressure gauges that were calibrated to ±0.1% of full-scale reading. A variation of ±0.1% would result in an error in *K* of ±0.08%. The power measurement consisted of independent determinations of both voltage and current. The maximum error of the voltage measurement was ±0.06%, whereas that for current was ±0.12%.

The measurements used to deduce the cell constant contribute an error of ±0.18%, based upon a maximum measurement error of ±7 parts in 100,000. Finally, heat loss errors, which were kept to a minimum through design, were estimated to result in an error of ±0.1%.

The total error for which corrections cannot be applied was therefore calculated to be ±1.06% or between 5.5×10^{-5} and 6.5×10^{-5} W/cm-deg, depending upon the value of *K*.

The single error for which correction of experimental results was possible is concerned with the placement of the thermocouple probes. Through design limitations, thermocouples could not be placed directly at the surface of the liquid. This finite distance contributed errors of from 1.35–1.60%, depending upon the value of *K* which changed in relation to temperature and pressure of the fluid. The actual calculation of *K* for the liquid was accomplished using the formula:

$$2\pi L \Delta T = VI\left[\frac{\ln\dfrac{r_0}{r_0 - d_1}}{K_s} + \frac{\ln\dfrac{r}{r_0}}{K} + \frac{\ln\dfrac{r}{r + d_2}}{K_s}\right] \quad (4)$$

where

L = length of thermally conductive fluid path
T = total temperature drop observed experimentally
V = voltage drop across the heater
I = current through the heater
r_0 = internal radius of fluid annulus
r = external radius of fluid annulus
K = thermal conductivity of fluid
K_s = thermal conductivity of silver
d_1 = distance from inner thermocouples to inner surface of fluid
d_2 = distance from outer thermocouples to outer surface of fluid

In all calculations the thermal conductivity of silver, K_s, was taken as a constant, with respect to pressure and temperature, of 4.209 W/cm-deg, d_1 equal to 0.210 cm and d_2 equal to 0.292 cm.

Results

The corrected experimental results of the measurements are listed in Table I. The data can be represented as a function of temperature by the equation:

$$K = 5.5780 \times 10^{-3} + 4.249 \times 10^{-7} P + 2.223 \times 10^{-5} T - 1.797 \times 10^{-7} T^3 \quad (5)$$

Table I. Thermal Conductivity (10^{-5} W/cm-deg) for Temperatures of 1.83–31.70°C and Pressures to 1400 Bars as Measured by Iron-Constantan and Chromel-Constantan Thermocouples

	I[a]				II[b]			
	Temperature, °C							
Press, bars	1.83	10.32	20.28	30.28	1.86	11.68	21.76	31.70
10	563.0	580.5	597.0	611.0	559.0	580.0	595.5	610.0
200	572.0	588.0	605.0	618.0	568.0	589.5	604.0	619.0
400	580.5	597.5	613.5	627.5	577.5	598.5	611.5	627.5
600	589.0	606.0	622.0	635.0	585.5	607.0	621.0	635.5
800	597.0	614.0	630.5	643.5	594.5	615.5	628.5	643.5
1000	604.0	623.5	638.0	653.0	604.0	622.0	639.0	652.0
1200	612.0	630.0	647.0	659.5	613.0	632.0	648.5	660.5
1400	[c]	639.5	654.5	668.5	[c]	642.0	655.5	669.0

[a] Measured by iron–constantan thermocouples. [b] Measured by chromel–constantan thermocouples. [c] Leaking seals, no reading taken.

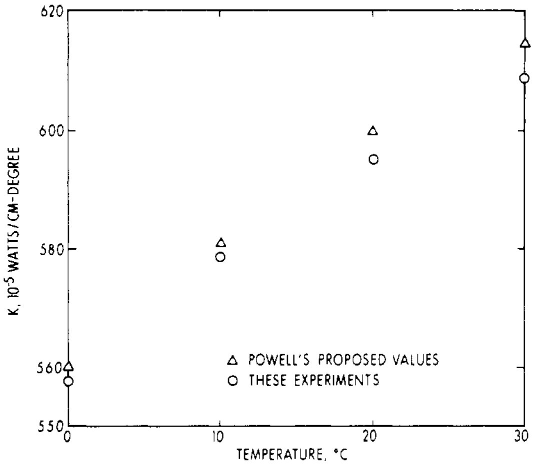

Figure 3. Comparison of Powell's proposed values for thermal conductivity of pure water at atmospheric pressure with values extrapolated from experimental results

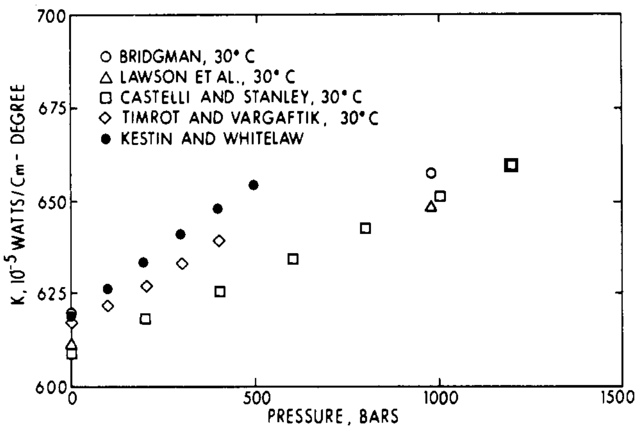

Figure 4. Comparison of historic pressure data at 30°C with experimental results

where K is given in W/cm-deg, P is the pressure in bars, and T is the temperature in degrees centrigrade. The values generated by this equation have a standard error of $\pm 1.5 \times 10^{-5}$ W/cm-deg or ±0.25% from the experimental data.

Discussion

Direct comparison of the data given by Equation 5 with that reported in the literature is only partly possible because most data for high pressure cover higher temperature ranges, and that for lower temperatures is restricted to low pressures.

Powell's (*5*) review and analysis of all the atmospheric pressure determinations has resulted in a set of "most probable" values for water. These data are shown in Figure 3 in comparison to our atmospheric values as determined from Equation 5. Our results are systematically about 0.5–1% lower than those "most probable" values cited by Powell. Although the origin of this discrepancy is unknown, no special effort was made to resolve this difference since we are primarily concerned with the effect of pressure on the thermal conductivity.

Previous experimental determinations of the thermal conductivity of water at high pressure have been conducted by Timrot and Vargaftik (*8*), Bridgman (*1*), and Lawson et al. (*3*); however, the overlap with our data is sparse. Figure 4 shows the data of Timrot and Vargaftik (*8*), Bridgman (*1*) [corrected in accordance with the recommendations of Riedel (*6*)], Lawson et al. (*3*), and our results for a temperature of 30°C.

Included in Figure 4 are the recommended values of thermal conductivity of water proposed by the Sixth International Conference on the Properties of Steam as reported by Kestin and Whitelaw (*2*). These values were calculated from a formula that covers the pressure range from saturation to 500 bars and temperatures from 0° to 300°C to a tolerance of ±2%. This tolerance just incorporates our values at atmospheric pressure, but as the pressure is increased, the discrepancy between our data and the values computed from the equation of Kestin and Whitelaw increases (Figure 4).

The reason for this behavior is that the Kestin and Whitelaw equation is designed to cover a large, nonlinear range of thermal conductivity. This possibly sacrifices some accuracy at the low end of the temperature scale, which is of but limited interest to power engineers, for greater accuracy at higher temperatures. Also, the data on which the equation is based are unstated.

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Vaporization Characteristics of 9-Phenylanthracene

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Equilibrium vapor pressures of solid (352–428K) and liquid (435–507K) 9-phenylanthracene were derived from torsion effusion and vapor-phase spectrophotometric absorbance measurements. The condensation coefficient on the solid was virtually unity. Molar absorptivities of the vapor were evaluated, and thermodynamic constants for the vaporization process were derived.

In connection with their studies of the solubilization of a series of similar hydrocarbons in DNA solutions, Craig and Isenberg (*5*) expressed an interest in the vaporization thermodynamics of 9-phenylanthracene. We also considered the kinetics of vaporization of such a large molecule to be of general interest and have undertaken a torsion effusion and a spectrophotometric study of the vapor pressure as a function of temperature. The large value of the molar absorptivity of the molecule in the vicinity of 242 mμ provides an opportunity for study of the temperature dependence of the absorbance of the saturated vapor at concentrations also suitable for effusion studies. By substantial variation of effusion orifice areas, information can be derived about the magnitude of the condensation coefficient on the solid; thermodynamic data derived from the two methods may be compared for consistency and provide a further test of the reliability of the effusion method (*20*).

Experimental

The torsion effusion apparatus was described previously (*15, 19*). Pyrex effusion cells were suspended by 1 or

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