Table IV. Viscosity as Function of Temperature

$\log_{10} \eta = A + B/T$

Substance	A	B	Temp range, K	SD A	SD B
$Ge(CH_3)_4$	−3.4620	708.10	277–304	0.00199	7.3825
$Ge(C_2H_5)_4$	−3.1660	842.11	278–337	0.00738	11.046
$Ge(C_3H_7)_4$	−4.6319	1445.9	277–341	0.01191	14.924
$Ge(C_4H_9)_4$	−6.0376	2114.5	276–339	0.02381	32.207
$Ge(C_5H_{11})_4$	−6.4937	2396.9	276–338	0.03857	55.607
$Ge(C_6H_{13})_4$	−6.5884	2509.0	277–338	0.C2687	39.901

Table V. Refractive Index and Dielectric Constant

Substance	Refractive index, 293.2K	Dielectric constant, 297.2K
$Ge(CH_3)_4$	1.3985[a]	1.817
$Ge(C_2H_5)_4$	1.4430	1.971
$Ge(C_3H_7)_4$	1.4510	1.921
$Ge(C_4H_9)_4$	1.4561	2.334
$Ge(C_5H_{11})_4$	1.4592	2.299

[a] Measured at 277.2K.

$Ge(C_6H_{13})_4$: 276.6, 12.46; 284.0, 9.524; 289.8, 7.874; 296.5, 6.345; 302.1, 5.425; 313.0, 4.006; 318.7, 3.567; 326.0, 3.024; 331.8, 2.696; 338.2, 2.379.

Results. Leasts-squares fits of the experimental data to the equation:

$$\log_{10} \eta = A + B/T \qquad (5)$$

are presented in Table IV.

Refractive index and dielectric constant. Refractive indices (measured at 5.08726×10^{14} sec^{-1}: Na D-line) of $Ge(CH_3)_4$, $Ge(C_2H_5)_4$, $Ge(C_3H_7)_4$, $Ge(C_4H_9)_4$, and $Ge(C_5H_{11})_4$ were obtained from a Bausch and Lomb refractometer (cat. no. 33-45-58) (7, 8). The dielectric constants of these compounds (measured at 1592 cps) were obtained from a Wayne Kerr Bridge, Model 201, used with a parallel plate cell. Calibration of the parallel plate cell was accomplished with spectroscopic grade benzene. For both refractive indices and dielectric constant observations, control and measurement of the temperature are the same as described in the Liquid Density section.

Data. Refractive indices and dielectric constants are presented in columns 1 and 2, Table V.

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Vapor Pressure of Biphenyl Near Fusion Temperature

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A chromatographic method has been used in a preliminary study (by use of a flow vaporizer) of the vapor pressure of solid and liquid biphenyl at temperatures close to (above and below) the melting point of the solid. The results for the solid are too low. However, the data indicate that the method is feasible, with proper care to equilibration and to temperature measurements.

Data on the pressure of liquid biphenyl are extensive and probably reliable, except for an absence of data near the freezing point. There have been no recent reports of measurements. The numbers given in "Handbook of Chemistry and Physics" (7) are taken from the 1947 compilation of Stull (5) for which the most recent

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sources of data on biphenyl were papers published in 1929 and 1930. The vapor pressure of the solid has been measured less often but more recently (1, 2, 4). The most precise work was done by Bradley and Cleasby (1) over the temperature range, 15.05–40.55°C. Timmermans (6) quotes the results in his 1965 volume. Bradley and Cleasby used an effusion method. A slightly higher temperature (46°C) was reached in the work of Bright (2). This is still some 24° below the melting point. It is clearly desirable to extend data on the solid up to the melting point.

We have used chromatographic determination of biphenyl concentrations in studies of its pyrolysis (3). Although it was not essential in that study to know the vapor pressure, the fact that a flow vaporizer was in the system suggested the possibility of saturating the flow and thus determining vapor pressures. The present data were taken mainly to assess the *feasibility* of using this method to determine the vapor pressure of the solid at temperatures within 20° of the melting point.

A biphenyl bubbling cell was constructed by use of a fritted disk immersed in biphenyl. The entire cell was maintained at constant temperature in a hot water thermostat, the temperature of which was measured to ±0.1°C with a mercury thermometer. Helium gas picked up biphenyl vapor in bubbling through the cell. Heating tape all along the course prevented the vapor from condensing before it entered a three-way heated valve (Carle Instrument Co.). The valve was connected to a gas chromatographic oven (F & M Model 700 gas chromatograph). Carrier gas (helium) passed at all times through one or the other of the two coils of the valve. One of the original coils (⅟₁₆-in. diameter) was replaced by a larger diameter loop made of copper tubing that had a volume of 10.5 cc. This loop was used for direct sampling of biphenyl vapor in the carrier gas stream. The chromatograph oven was thermostated at 150°C.

"Highest purity" grade biphenyl, purified further by sublimation, was used in the experiments. Vaporization of biphenyl was carried out at four thermostat temperatures from 53.0° to 81.0°C. Two temperatures were below the melting point; one was slightly above the mp, and one was well above it. Helium was able to penetrate through the biphenyl even when it was solid. Flow rates of helium were varied to test for stream saturation. A 4-ft silicone

gum (S.E.-30) column was used at 150°C; the biphenyl peak showed a retention time of 3.75 min. The thermocouple detector sensitivity was determined by injection of 5 μl of a standard solution of biphenyl in benzene. Limitations of the detector sensitivity set a lower limit of about 0.1 torr on vapor-pressure measurements.

The experimental vapor pressure data are given in Table I and are plotted in Figure 1 together with data from other sources. Our results are consistent with the data of Seki and Suzuki (4) and lie fairly close to the equation for the solid given in "Handbook of Chemistry and Physics" (7). The Bradley and Cleasby data extrapolate to give pressures about 40% above ours. The data of Bright (2) are markedly below other results.

The figure reveals that our results for the solid, and all others as well [with the possible exception of the results of Bradley and Cleasby (1)], probably are too low, since they do not join the (linearly) extrapolated vapor-pressure line for the liquid at the melting point. The actual discrepancy is uncertain because there will be some curvature in the liquid line. In the present case, this discrepancy strongly suggests a heat-transfer effect causing vaporization temperatures of the solid to be somewhat lower than the thermostat temperatures. This effect may explain why the point reported at 344.2K agrees with lower temperature points for the solid and falls below the liquid line.

The heat-transfer problem presumably did not arise for the single point obtained for the liquid because convective heat transfer and stirring by the bubbles greatly facilitated temperature equalization between the liquid and the surroundings. The discrepancy could, however, also be attributable to a low vaporization coefficient for the solid, whereas that for the liquid should be close to unity. Neither explanation is entirely convincing since variation

Table I. Experimental Results

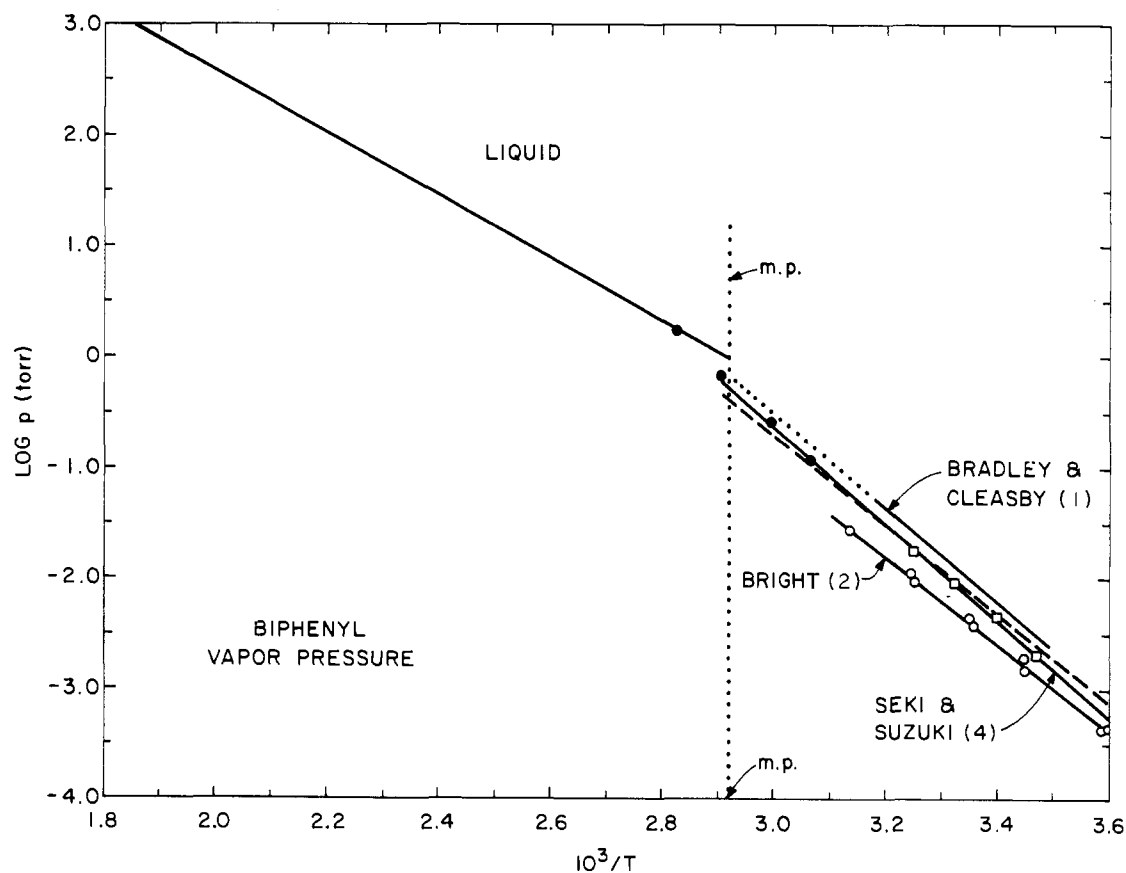| T, K, bath	Vp, torr
326.2	0.12
334.2	0.26
344.2	0.69
354.2	1.65

Figure 1. Biphenyl vapor-pressure data. Liquid line from Stull (5). Dashed line: equation for solid from ref. 7. Solid circles: present data. Other sources of data on solid are indicated on figure

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.

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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:

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

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:

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

Rearranging Equation 2 gives

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

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.