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# Thermal Conductivity and Heat Capacity of Liquid Toluene at Temperatures Between 255 and 400 K and at Pressures up to 1000 MPa

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The thermal conductivity $\lambda$ and heat capacity $c_p$ of liquid toluene have been measured by the ac-heated wire method up to 1000 MPa in the temperature range from 255 to 400 K. The total error of thermal conductivity measurements is estimated to be about 1%, and the precision 0.3%. The heat capacity per unit volume, $\rho c_p$, obtained directly from the experiment is uncertain within 2 or 3%. The $\lambda$ vs p isotherms are found to cross one another at approximately 700 MPa. The minima in the pressure (or volume) dependence of $c_p$ of toluene are evident at all temperatures investigated.

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**KEY WORDS:** ac-heated wire method; heat capacity; high pressure; thermal conductivity; toluene.

## 1. INTRODUCTION

For many years, toluene has been used as a reference fluid in calibrations of various thermal conductivity cells and probes. At the present time, extensive data on its thermal conductivity are available over a wide temperature range. A few investigations have also been reported recently extending the measurements to higher pressures [1–3].

However, another important thermal quantity, the heat capacity, has been measured with less success, and no reliable high-pressure data on toluene (or any other liquid) have been obtained so far.

In our experiments we applied a version of the ac-heated wire method [4–6] allowing both the thermal conductivity and the heat capacity of

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liquids to be measured reliably over a wide temperature and pressure range with a high degree of accuracy. Toluene was naturally selected as a liquid to be studied since a direct comparison with the results published in the literature made it possible to substantiate the merits of the new method more definitely.

## 2. EXPERIMENTAL

Although the cells designs in the ac-heated wire method and the well-known transient hot-wire method are practically identical, the measuring procedures are quite different. A low-frequency (20- to 300-Hz) alternating current passing through the thin metal wire makes its temperature oscillate. The amplitude of oscillations $|\theta|$ and their phase shift $\varphi$ relative to the heating ac current are determined primarily by the thermal properties of the surrounding fluid.

It should be noted that the production and measurement of the temperature waves can be accomplished in several ways. Filippov [7] heated the wire by alternating current of frequency $f$ and measured the resulting ac voltage of triple frequency $3f$ developed across the wire. Since the low-frequency oscillations of amplitudes of about 100 $\mu$V are difficult to measure accurately, we used an alternative technique. In the present experiment, the wire of resistance $R_0$ was heated simultaneously by direct current $I_0$ and alternating current $I \sin \omega t$, with $|I| \ll I_0$. Under these conditions the temperature of the wire oscillated with frequency $\omega$ relative to its mean value, which typically exceeded the environmental temperature by about 2 K due to dc heating. The amplitudes of temperature waves in the liquid near the surface of the wire were estimated to be about 50 mK or less. From the energy balance equation the following relations for the temperature amplitude $|\theta|$ and phase $\varphi$ can be derived:

$$\begin{aligned} \frac{|\theta|}{\theta_0} &= \left[1 + 4\frac{B}{Z}\frac{N_1}{N_0}\cos\left(\phi_1 - \phi_0 + \frac{\pi}{4}\right) + 4\left(\frac{B}{Z}\frac{N_1}{N_0}\right)^2\right]^{-1/2} \\ \tan\varphi &= -\frac{1 + 2(B/Z)(N_1/N_0)\cos[\phi_1 - \phi_0 + (\pi/4)]}{2(B/Z)(N_1/N_0)\sin[\phi_1 - \phi_0 + (\pi/4)]} \end{aligned} \qquad (1)$$

where $B = \rho c_p/\rho' c'_p$ is the ratio of heat capacities per unit volume of the liquid studied and the metal of which the wire is made (e.g., platinum), $N_1/N_0$ and $\phi_1 - \phi_0$ are the ratio of moduli and the difference of arguments of modified Bessel functions $K_0(zi^{1/2})$, $z = r_0(\omega \rho c_p/\lambda)^{1/2}$, $r_0$ is the radius of the wire, and $\theta_0 = 2I_0 \cdot I \cdot R_0/m' c'_p \omega$ is the normalizing factor corresponding to the temperature oscillation amplitude determined by the heat capacity of the wire $m'c'_p$.

In the presence of temperature oscillations the wire acquires an impedance [5]

$$Z = R_0 + A - iB \tag{2}$$

where $A = (I_0/I)(dR_0/dT)\,|\theta|\cos\varphi$ and $B = (I_0/I)(dR_0/dT)\,|\theta|\sin\varphi$.

The impedence of the equivalent circuit consisting of resistance $R$ and capacitance $C$ connected in parallel is equal to

$$Z_{\text{eq}} = (R - i\omega R^2 C)/[1 + (\omega RC)^2] \tag{3}$$

Comparing Eqs. (2) and (3) and taking into account that in our experiment $(\omega RC)^2 < 10^{-5}$, we obtain the expression relating the amplitude and phase of temperature oscillations with the electric quantities, whose values can be directly measured in the experiment

$$\frac{|\theta|}{\theta_0}\sin\varphi = \Lambda\frac{\omega^2 C}{2I_0^2}\left(\frac{R}{R_0}\right)^2 \tag{4}$$

where $\Lambda = m'c'_p/[(1/R_0)(dR_0/dT)]$. Thus, the values of thermal conductivity $\lambda$ and heat capacity per unit volume $\rho c_p$ can be obtained from Eqs. (1), (2), and (3) provided that the measurements were performed at two different frequencies, $\omega_1$ and $\omega_2$. The constant $\Lambda$ and radius $r_0$ of the wire are obtained from special measurements. When the cell is placed in vacuum the amplitude of temperature oscillations is determined entirely by the heat capacity of the wire $m'c'_p$ and the value of $\Lambda$ can be easily calculated. The radius $r_0$ is found from the diffraction pattern formed on a screen by a laser beam crossing the wire. The details of these auxiliary experiments can be found elsewhere [6, 8].

Figure 1 shows schematically the design of the cell. Two platinum wires (1 and 2) (one 40 and the other 8 mm in length) of 20-$\mu$m diameter are suspended inside two bores drilled in a copper block (3) and having an internal diameter of 2 mm. The wires are switched in the adjacent arms of the bridge to compensate longitudinal temperature gradients in the wire and the surrounding liquid. Since the temperature waves propagating radially from the wire surface completely fade away at distances of about 100 $\mu$m, small bends in the wire have no effect and no special efforts are therefore needed to keep the wire taut.

To measure the electric quantities appearing on the right side of Eq. (4), the bridge should be balanced in both ac and dc modes. In the first case we obtain the equivalent capacity $C$ of the cell and the real component

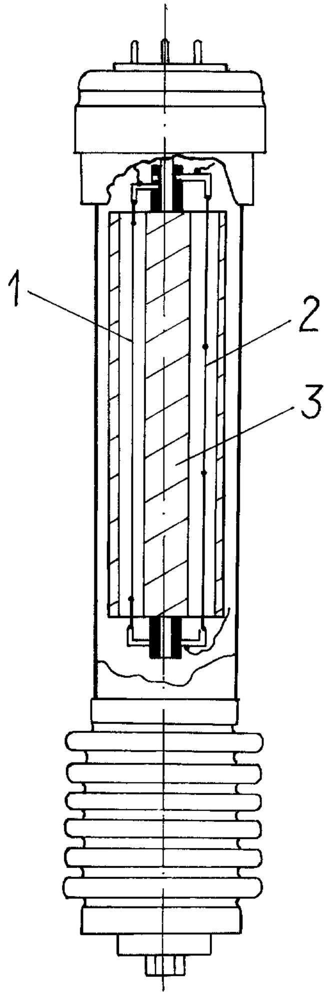

**Fig. 1.** Design of the ac-heated wire cell. (1, 2) Platinum wires; (3) copper block.

of its impedance $R$. In the latter case we measure the active resistance of the wire $R_0$.

The present technique entirely eliminates the problem of free convection. It was shown [9] that in the case of dc heating of the wire suspended along the axis of a tube whose diameter varied from 3 to 13 mm, free convection set in whenever the product of the Grashof and Prandtl numbers exceeded 1700. In our experiments the product $Gr \cdot Pr$ was always below

1000 due to small deviations of the mean temperature of the wire from the entironmental temperature. Besides, as the earlier ac-heated wire measurements at atmospheric pressure [10] have shown, the thermal properties of toluene turn out to be independent of the product $Gr \cdot Pr$ in the range from $10^3$ to $10^5$. There is no doubt that at $Gr \cdot Pr = 10^4$ free convection is well developed in the cells of this geometry. But as mentioned before, the temperature waves rapidly attenuate across a layer of fluid adhered to the surface of the wire and at rest with respect to it. In other words, the actual measurements involve only a thin motionless layer of fluid in which no convection can exist. Accordingly, the duration of a single measurement is not restricted in this method.

The effect of radiative heat transfer on thermal conductivity measurements by the ac-heated wire method was analyzed in detail earlier [11, 12]. The authors pointed out that in most cases this contribution is well below 0.1% up to the temperature of 400 K provided that the ac frequency lies in the range from 20 to 200 Hz.

The method described is very convenient to apply at high pressures, as the parameters of the cell vary with pressure to a small degree. The compressibility and pressure and temperature dependence of resistance of platinum are known [13] and can be easily allowed for. The heat capacity of pure metals is known [14] to diminish by approximately 1% at 3GPa. This value is too small to affect appreciably the accuracy of thermal conductivity measurements in liquids but can raise the apparent heat capacity as much as 1.5% at 1000 MPa.

The high-pressure cell was assembled as follows. Having been filled with degassed toluene under vacuum and sealed, the cell was fixed to a plug provided with electrical leads and placed in a high-pressure vessel. The temperature of the vessel immersed in an oil bath was measured with a standard resistance thermometer and controlled to within ±50 mK. The vessel was connected to a high-pressure intensifier by a capillary tube made of maraging steel with an inside diameter of 2 mm and an outside diameter of 6 mm. Petroleum ether served as a pressure-transmitting medium. The pressure was measured with a manganin gage celibrated against a standard piston gage. The overall error of pressure measurements did not exceed 0.4%.

The toluene sample studied was characterized by a purity better than 99.5%. At 20°C its density was 866.5 $kg \cdot m^{-3}$ and the refractive index was 1.4961.

## 3. EXPERIMENTAL RESULTS

The raw experimental data on thermal conductivity $\lambda$ and heat capacity per unit volume $\rho c_p$ of toluene are presented in Table I.

The temperature dependence of $\lambda$ of toluene along the saturation curve from 255 to 400 K can be described by the quadratic equation

$$\lambda_0 = 0.2333 - 3.956 \times 10^{-4}\, T + 1.477 \times 10^{-7}\, T^2 \qquad (5)$$

with the average deviation 0.15 and the maximum deviation 0.36%. Figure 2 illustrates the relative deviations of literature values from Eq. (5). The data of Rastorguev and Pugach [15] obtained by the method of coaxial cylinders lie a few percent higher, with the difference tending to increase at higher temperatures. The obvious cause of such a discrepancy is the effect of radiative heat transport inherent in practically all steady-state measurement methods. The early transient hot-wire measurements [16] gave the lower values differing by 2 to 7%, while the more recent data [17, 18] are only about 2% higher. A still better agreement is observed with the results of Filipov et al. [19] and, especially, of Spirin [20], who used a square-wave technique.

To make the present high-pressure data more convenient to compare

**Table I.** Thermal Conductivity and Heat Capacity per Unit volume of Toluene

| $p$ (MPa) | $\lambda$ ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$) | $\rho c_p$ ($\mathrm{kJ \cdot m^{-3} \cdot K^{-1}}$) |
|---|---|---|
| | $T = 255.5$ K | |
| 0 | 0.1417 | 1417 |
| 24.1 | 0.1485 | 1430 |
| 68.0 | 0.1587 | 1453 |
| 116.0 | 0.1677 | 1481 |
| 185.7 | 0.1794 | 1518 |
| 252.3 | 0.1884 | 1558 |
| 304.7 | 0.1946 | 1594 |
| 356.8 | 0.2005 | 1619 |
| | $T = 272.5$ K | |
| 0 | 0.1365 | 1426 |
| 36.6 | 0.1464 | 1444 |
| 76.7 | 0.1572 | 1465 |

Table I. *(Continued)*

| $p$ (MPa) | $\lambda$ $(\mathrm{W \cdot m^{-1} \cdot K^{-1}})$ | $\rho c_p$ $(\mathrm{kJ \cdot m^{-3} \cdot K^{-1}})$ |
|---|---|---|
| 137.3 | 0.1684 | 1499 |
| 179.3 | 0.1766 | 1527 |
| 248.7 | 0.1870 | 1570 |
| 333.5 | 0.1979 | 1615 |
| 402.2 | 0.2057 | 1651 |
| 494.9 | 0.2150 | 1699 |
|  | $T = 300.6$ K |  |
| 0 | 0.1282 | 1461 |
| 13.4 | 0.1330 | 1465 |
| 32.0 | 0.1393 | 1474 |
| 57.3 | 0.1464 | 1489 |
| 88.2 | 0.1544 | 1504 |
| 112.5 | 0.1599 | 1526 |
| 142.7 | 0.1662 | 1538 |
| 184.1 | 0.1737 | 1570 |
| 255.1 | 0.1853 | 1618 |
| 300.7 | 0.1926 | 1631 |
| 354.0 | 0.1988 | 1675 |
| 452.6 | 0.2110 | 1715 |
| 509.4 | 0.2178 | 1740 |
| 605.4 | 0.2262 | 1795 |
| 704.2 | 0.2353 | 1827 |
| 816.5 | 0.2452 | 1857 |
| 902.6 | 0.2510 | 1899 |
|  | $T = 326.2$ K |  |
| 0 | 0.1199 | 1498 |
| 15.4 | 0.1260 | 1503 |
| 32.8 | 0.1322 | 1510 |
| 57.3 | 0.1398 | 1522 |
| 81.5 | 0.1463 | 1543 |
| 176.5 | 0.1677 | 1609 |
| 232.3 | 0.1782 | 1645 |
| 312.7 | 0.1911 | 1691 |
| 409.6 | 0.2038 | 1741 |
| 497.7 | 0.2150 | 1790 |
| 635.4 | 0.2294 | 1851 |
| 773.5 | 0.2419 | 1910 |
| 856.6 | 0.2485 | 1947 |
| 928.5 | 0.2545 | 1963 |
| 993.5 | 0.2592 | 1988 |

Table I. *(Continued)*

| $p$ (MPa) | $\lambda$ $(\mathrm{W \cdot m^{-1} \cdot K^{-1}})$ | $\rho c_p$ $(\mathrm{kJ \cdot m^{-3} \cdot K^{-1}})$ |
|---|---|---|
| $T = 354.5$ K | | |
| 0 | 0.1116 | 1523 |
| 12.2 | 0.1171 | 1529 |
| 39.1 | 0.1272 | 1553 |
| 91.8 | 0.1428 | 1600 |
| 141.5 | 0.1551 | 1636 |
| 188.0 | 0.1652 | 1670 |
| 291.1 | 0.1841 | 1741 |
| 400.6 | 0.2006 | 1803 |
| 619.2 | 0.2271 | 1912 |
| 744.5 | 0.2397 | 1962 |
| 916.5 | 0.2548 | 2035 |
| 986.5 | 0.2603 | 2058 |
| $T = 381.6$ K | | |
| 0 | 0.1036 | 1573 |
| 34.0 | 0.1184 | 1602 |
| 74.8 | 0.1323 | 1625 |
| 126.8 | 0.1469 | 1660 |
| 188.0 | 0.1608 | 1720 |
| 248.7 | 0.1730 | 1760 |
| 303.9 | 0.1829 | 1797 |
| 406.2 | 0.1991 | 1858 |
| 495.3 | 0.2114 | 1905 |
| 605.4 | 0.2250 | 1955 |
| 700.1 | 0.2352 | 1997 |
| 796.0 | 0.2447 | 2041 |
| 885.3 | 0.2530 | 2072 |
| 983.6 | 0.2614 | 2106 |
| $T = 401.5$ K | | |
| 3.5 | 0.1001 | 1580 |
| 16.9 | 0.1064 | 1610 |
| 54.2 | 0.1211 | 1633 |
| 126.8 | 0.1429 | 1698 |
| 197.2 | 0.1596 | 1750 |
| 369.3 | 0.1913 | 1873 |
| 507.0 | 0.2111 | 1953 |
| 707.8 | 0.2352 | 2050 |
| 789.5 | 0.2440 | 2077 |
| 907.5 | 0.2550 | 2128 |
| 991.5 | 0.2625 | 2151 |

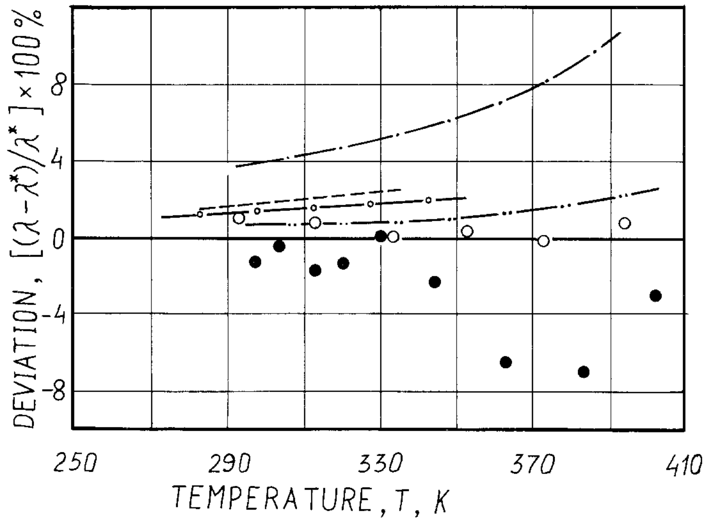

**Fig. 2.** Deviations of experimental thermal conductivity data from the values $\lambda^*$ obtained in the present work and interpolated by Eq. (5). (–•–•–) Ref. 15; (–––––) Ref. 17; (–∘–∘–) Ref. 18; (–•••–) Ref. 19; (●) Ref. 16; (○) Ref. 20.

with the earlier results, fits have been made to the Hayward-type equation for each experimental isotherm:

$$\lambda_p = \frac{\lambda_0}{1 + p/(D_0 + D_1 p + D_2 p^2 + D_3 p^3)} \tag{6}$$

In this equation $\lambda_0$ and $\lambda_p$ are the thermal conductivities at atmospheric pressure and pressure $p$, respectively, and $D_0$, $D_1$, $D_2$, and $D_3$ are the constants which provide the best fit of the experimental data. The values of the coefficients in Eq. (6) are listed in Table II together with the average and maximum deviations of the experimental data from Eq. (6). The maximum deviations seem to be within the experimental uncertainty for all isotherms.

Figure 3 shows that with the exception of Rastorguev and Pugach [15], the earlier authors reported values agreeing with the present results to within 5%. A very good agreement is observed with the data obtained by Kashiwagi and co-workers [2] and with the most recent data by Nieto de Castro et al. [3]. The deviations are about 1% and less at all temperatures for $p > 50$ MPa.

The raw atmospheric-pressure data on the heat capacity per unit volume are adequately described by a linear equation,

$$\rho c_p = 1098 + 1.2109T \tag{7}$$

**Table II.** Coefficients of Interpolation Eq. (6) for the Thermal Conductivity of Toluene

| $T$ (K) | $\lambda_0$ ($W \cdot \mathrm{m}^{-1} \cdot \mathrm{K}^{-1}$ | $D_0$ (MPa) | $D_1$ | $-D_2 10^3$ ($\mathrm{MPa}^{-1}$) | $D_3 10^6$ ($\mathrm{MPa}^{-2}$) | Av. dev. (%) | Max. dev. (%) |
|---|---|---|---|---|---|---|---|
| 255.5 | 0.1417 | 450.48 | 2.9151 | 3.8995 | 4.9145 | 0.08 | 0.17 |
| 272.5 | 0.1365 | 468.73 | 1.5883 | 1.3026 | 1.8232 | 0.15 | 0.39 |
| 300.6 | 0.1282 | 340.52 | 2.0840 | 0.7976 | 0.3721 | 0.13 | 0.33 |
| 326.2 | 0.1199 | 294.93 | 1.9082 | 0.5972 | 0.2554 | 0.13 | 0.31 |
| 354.5 | 0.1116 | 246.42 | 1.8952 | 0.7479 | 0.3557 | 0.21 | 0.41 |
| 381.6 | 0.1036 | 216.93 | 1.7343 | 0.5366 | 0.2391 | 0.14 | 0.24 |
| 401.5 | 0.0985 | 205.28 | 1.6375 | 0.4129 | 0.1690 | 0.10 | 0.20 |

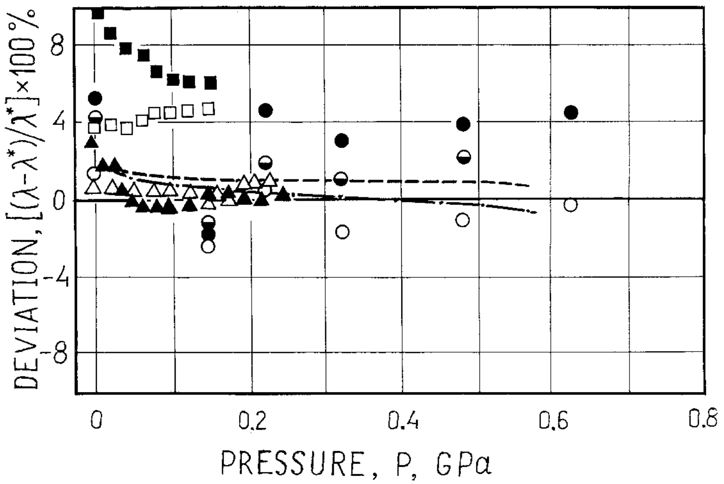

Fig. 3. Deviations of experimental high-pressure thermal conductivity data from the values $\lambda^*$ obtained in the present work and interpolated by Eq. (6). (□) 293 K [15]; (■) 393 K [15]; (○) 304.0 K [1]; (○) 334.6 K [1]; (●) 364.7 K [1]; (△) 273 K [2]; (▲) 373 K [2]; (---) 308 K [3]; (-·-·-) 360 K [3].

where $\rho c_p$ is in kJ · m$^{-3}$ · K$^{-1}$. In the temperature range from 250 to 400 K the average deviation from Eq. (7) is equal to 0.39 and the maximum deviation is 0.74%.

The high-pressure experimental values of $\rho c_p$ have been fitted by a cubic polynomial equation,

$$\rho c_p = K_0 + K_1 p + K_2 p^2 + K_3 p^3 \tag{8}$$

whose coefficients are listed in Table III.

To evaluate the specific heat capacity $c_p$, we used the high-pressure compressibility data obtained for toluene up to 250 MPa [21] and extrapolated to higher pressures by means of the Tait-type equation

$$\rho(p, T) = \frac{1144.2 - 0.9468\,T}{1 - 0.0945 \ln[1 + (p/1381.5)\,e^{8.62 \times 10^{-3}\,T}]} \tag{9}$$

where $\rho$ is in kg · m$^{-3}$, $p$ is in MPa, and $T$ is in K. The average deviation of the density data by Kashiwagi et al. [2] from Eq. (9) does not exceed 0.25% within the experimental range of pressure and temperature.

**Table III.** Coefficients of Interpolation Eq. (8)[a]

| $T$ | $K_0$ | $K_1$ | $K_2 \times 10^4$ | $K_3 \times 10^7$ | SD |
|---|---|---|---|---|---|
| 255.5 | 1418 | 4.859 | 4.956 | −7.46 | 2.2 |
| 272.5 | 1425 | 5.373 | 2.697 | −4.83 | 1.9 |
| 300.6 | 1453 | 6.744 | −2.051 | — | 6.3 |
| 326.2 | 1490 | 6.996 | −2.008 | — | 4.0 |
| 354.5 | 1520 | 8.907 | −5.350 | 1.87 | 2.5 |
| 381.6 | 1569 | 8.420 | −3.738 | 0.73 | 5.0 |
| 401.5 | 1584 | 9.467 | −4.963 | 1.20 | 5.4 |

[a] The units of the quantities are as follows: $T$ in K, $K_0$ in $\mathrm{kJ \cdot m^{-3} \cdot K^{-1}}$, $K_1$ in $\mathrm{kJ \cdot m^{-3} \cdot K^{-1} \cdot MPa^{-1}}$, $K_2$ in $\mathrm{kJ \cdot m^{-3} \cdot K^{-1} \cdot MPa^{-2}}$, $K_3$ in $\mathrm{kJ \cdot m^{-3} \cdot K^{-1} \cdot MPa^{-3}}$, and SD in $\mathrm{kJ \cdot m^{-3} \cdot K^{-1}}$.

## 4. DISCUSSION

The thermal conductivity of all liquids increases with pressure, with the value of derivative $(\partial\lambda/\partial p)_T$ increasing with temperatures. As the temperature derivative $(\partial\lambda/\partial T)_{p=0} < 0$ (with the exception of water), one can expect the isotherms to come closer to one another at elevated pressures. Bridgman [13] was the first to report the actual intersection of isotherms $\lambda = \lambda(p)$. According to his analysis, $\partial\lambda/\partial T$ reverses its sign around 300 MPa for all liquids studied. Since his experiments were carried out by the method of coaxial cylinders and the total error of his measurements was probably large due to the above-mentioned effects of radiative heat transfer, Bridgman's principal conclusion about the isotherm intersection was not universally accepted. The qualitative confirmation came from Kandiyoti and co-workers [1], who observed an increase in isobaric thermal conductivity of toluene with temperature at $p > 300$ MPa, although the values of $\lambda$ proved to be 20 to 30% lower than Bridgman's.

The analysis of our data revealed that at pressures between 700 and 750 MPa, the values of $\lambda$ became equal within the experimental error for all isotherms ranging from roughly 300 to 400 K. At 1000 MPa the thermal conductivity at 401.5 K turned out to be 2% higher than that at 300.6 K, i.e., $\partial\lambda/\partial T$ became positive.

Figure 4 shows how the heat capacity of toluene varies with density $\rho$ at four temperatures. The values of $\rho$ have been calculated from Eq. (9). All curves have shallow minima at a density of about $930\ \mathrm{kg \cdot m^{-3}}$. The isothermal $c_p$ vs $p$ relationship is also characterized with a minimum shifting from 100 to 250 MPa as the temperature goes from 255 to 400 K. Similar behavior was recently reported for *n*-heptane and *n*-octane [22].

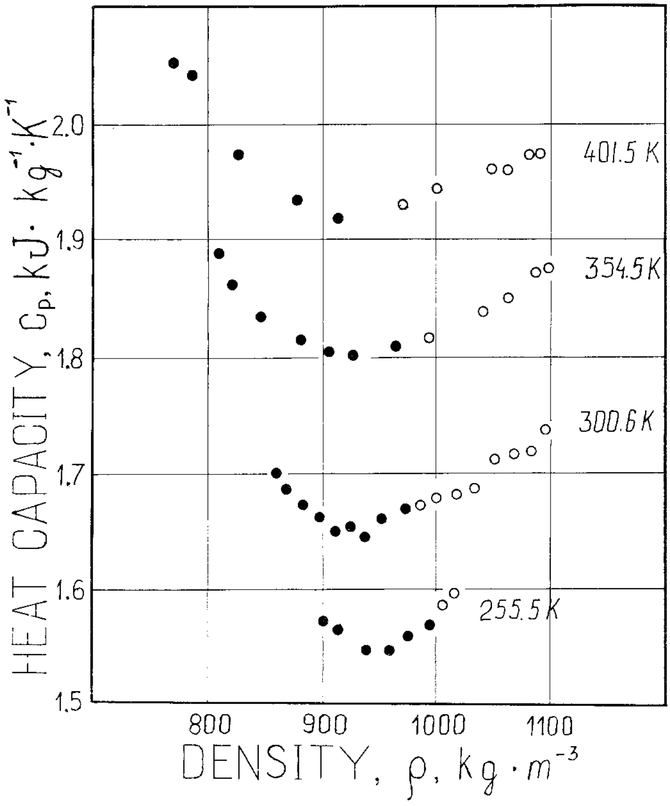

**Fig. 4.** Heat capacity of toluene as a function of density at various temperatures. (●) Experimental density values; (○) density values extrapolated by means of Eq. (9).

Bridgman reported the minima in $c_p$ vs $p$ curves for liquids over 70 years ago [23]. From the analysis of his compressibility data he obtained the change in heat capacity using the thermodynamic relation

$$\Delta c_p = -T \int_0^p (\partial^2 v/\partial T^2)_p \, dp \qquad (10)$$

The later attempts, however, to accomplish the integration of Eq. (10) using empirical equations of state $v = v(p, T)$ [24, 25] were incnclusive. At present the available $p$–$v$–$T$ data, as well as equations of state based on them, are probably inadequate to admit a meaningful determination of the second derivative $(\partial^2 v/\partial T^2)_p$ and any definite conclusion about the behavior of $c_p$ as a function of pressure. The measurements of heat capacity by the transient hot-wire method [25] also could not reveal any minima since the measurement errors were as large as 10%. Thus, our data seem to be the only proof of the existence of minima in the pressure (or density) dependence of the heat capacity of a liquid obtained directly from an experiment.

In the method used here the values of thermal conductivity and heat capacity of liquids are compatible in the sense that they are tied in a single system of equations. This means that the good agreement of thermal conductivity data mentioned above provides an indirect proof of the correctness of the pressure dependence of the heat capacity of toluene reported here.

The peculiar behavior of specific heat capacity is rather difficult to interpret quantitatively in terms of molecular theory. We suppose that at comparatively low pressures the reduction in free volume of a liquid impairs the external degrees of freedom of individual molecules, whereas further compression results in distortion of molecules, leading to a redistribution of internal degrees of freedom and an increase in the energy-storing capability of molecules. The superposition of these two trends may obviously cause the minima observed.

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