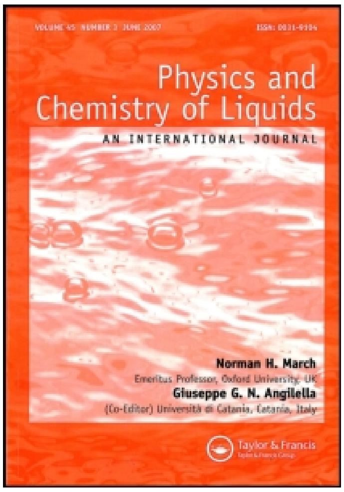

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The Effect of Pressure on the Sound Velocity and Density of Toluene and *n*-heptane up to 2600 bar

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The Effect of Pressure on the Sound Velocity and Density of Toluene and *n*-heptane up to 2600 bar

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The sound velocity in toluene has been measured up to 2634 bar and at temperatures from 173 to 320 K using the pulse-echo overlap method. The sound velocity in *n*-heptane has been measured up to 2634 bar and at temperatures from 185 to 310 K by the phase comparison pulse-echo method. The density, the isothermal compressibility, the isobaric thermal expansion and the specific heat at constant pressure of both liquids have been evaluated from the measured sound velocity, following the method of Davis and Gordon. From a comparison of the calculated densities with those obtained previously from direct measurements, it is concluded that the method is very suitable for precise determination of liquid densities under elevated pressures.

1 INTRODUCTION

The ultrasonic measurement of sound velocity in liquids provides a simple means of the precise determination of a number of thermophysical properties whose determination by direct measurement is both tedious and difficult. Ultrasonic methods are also preferred to direct thermodynamical methods because of the simplicity and rapidity of the experimental procedure. Furthermore, the availability of modern computer facilities makes it possible to perform the numerical calculations which are necessary to extract the required data from the measured sound velocity without introducing additional errors. This paper reports the development of an ultrasonic apparatus for the measurement of sound velocity in liquids at high pressures up to 3 kbar and the use of velocity data for the precise determination of a number of important physical properties, namely the density, the isothermal compressibility, the isobaric thermal expansion coefficient and the specific heat at constant pressure. Toluene and *n*-heptane were chosen as a first test of the apparatus because these two organic compounds have previously been studied by other measuring techniques which makes it possible to compare the present method of measurement with other methods. In our opinion, the ultrasonic high pressure equipment will be very useful as a tool in the systematic investigation of the physical properties of a large number of organic liquids for which only scattered data are available.

2 APPARATUS

The ultrasonic apparatus, used for the measurement of sound velocity in toluene, is based on the pulse-echo overlap method described previously by Papadakis[1] and is operated at a frequency of 2 MHz. A sketch of the cell is shown in Figure 1. It is made of a hollow aluminium cylinder in which an X-cut quartz transducer (B) is fixed by clamping at the edges. A solid copper reflector (R) having a conical cavity (C) at the rear end plane is fixed at a distance of about 2 cm from the transducer. In order to eliminate back coupling from the opposite direction, an oil reservoir (D) with a total length of 4.5 cm is placed on one side of the transducer. The design of the ultrasonic cell is such

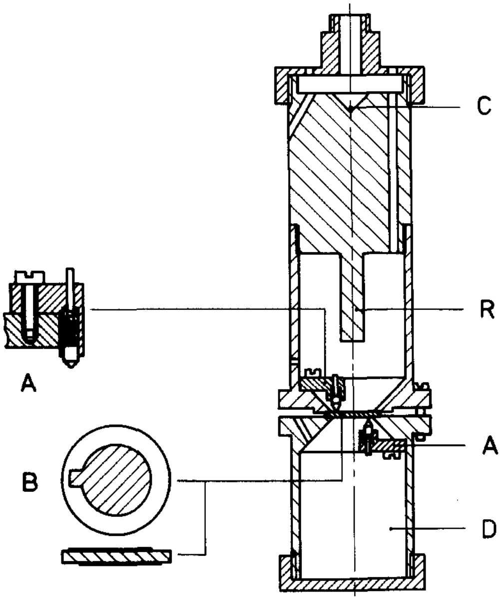

FIGURE 1 Ultrasonic apparatus for sound velocity measurements based on the pulse-echo overlap method.

that unwanted echoes coming from other directions reach the transducer only after the arrival of the second echo.

Each of the faces of the transducer is provided with an electrode of evaporated aluminium and the electrical contact with the electronic system is made by using a needle contact, pressed firmly on the electrode by means of a spring (see detail A, Figure 1). When an electrical pulse is applied to the electrodes, the transducer is excited into a thickness mode of vibration which produces a sound pulse in the liquid. The pulse travels through the liquid and, after reflection at the reflector, returns to the transducer, producing a detectable electrical signal: an echo. By adjusting the triggering frequency of the time base of an oscilloscope, it is possible to make two successive echoes overlap on the screen of the oscilloscope. The transit time, which is the time necessary for the pulse to travel from the transducer to the reflector, can be found from the measured trigger frequency and from which the sound velocity can easily be determined.

The pulse-echo overlap method, as it was originally used for the sound velocity measurement in toluene, has the disadvantage that there is a small phase change over the length of the pulse as a result of the distortion of the sound pulse when it is reflected at the front and at the reverse side of the transducer. This may cause an uncertainty in the measured trigger frequency and hence in the transit time. It seemed, therefore, worthwhile to develop a second ultrasonic apparatus for the sound velocity measurements in *n*-heptane which avoids the above-mentioned distortion of the sound pulse and which can also operate at 2 MHz.

This second ultrasonic apparatus is based on the phase comparison pulse-echo method first developed by Williams and Lamb.[2] However, a special feature of the present set up is the use of two reflectors placed at different distances from the quartz transducer as shown in Figure 2. At the start of the

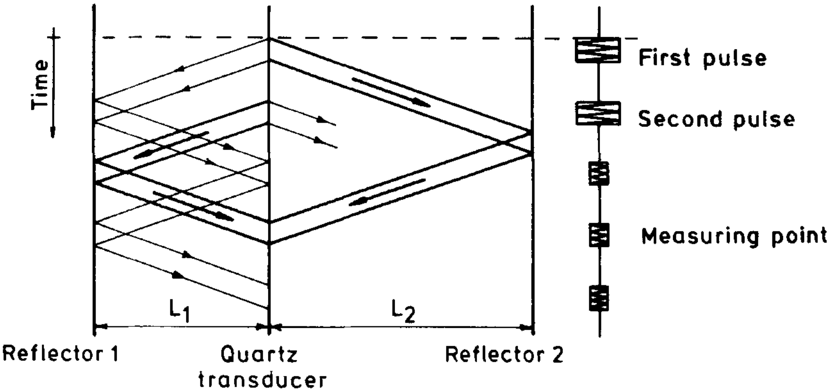

FIGURE 2 Basic principle of the phase comparison method with two reflectors.

cycle, a pulse is clipped from the continuous signal of a 2 MHz oscillator by means of a gate system and introduced in the medium. The pulse is reflected by both reflectors. After an appropriate time, a second pulse is clipped from the continuous signal and introduced in the medium such that the echo of the first pulse travelling the longer path and the echo of the second pulse travelling the shorter path coincide at their arrival at the quartz transducer. Therefore, when the amplitudes of the pulses are properly adjusted, the two pulses can annihilate each other completely at certain frequencies and the resulting signal displayed on an oscilloscope becomes zero. By measuring these frequencies with a counter, it is possible to determine the transit time and, hence, the sound velocity.

A sketch of the ultrasonic cell used for the sound velocity measurements in *n*-heptane is shown in Figure 3. Here also, the transmitter-receiver is an X-cut quartz crystal (A) which is clamped at its edge in a hollow copper cylinder (B). Two solid copper reflectors (R) are fixed in the cell at distances of, respectively, 4 and 6 cm from the transducer. Copper is chosen for this purpose since it has a sufficiently large acoustic impedance and, moreover, it has a good thermal conductivity which minimizes the temperature gradient in the cell. Also its thermal expansion and compressibility are well-known. The lengths of the reflectors are so chosen that unwanted reflections reach the transducer only after the arrival of the two echoes. Further, both end planes of the reflectors contain conical cavities (C) so that part of the signal, which is carried over to the reflector material, changes its direction and moves to-and-fro in the metal.

The electrical contact between the electronic system and the evaporated aluminium electrode on each of the faces of the transducer is made in a way similar to that of the previous cell used for sound velocity measurements in toluene. In the present set-up, the interference over the finite thickness of the quartz transducer occurs because of the special property of the piezo-electric effect. According to this, the difference in electrical potential between the two evaporated electrodes on the surface of the quartz transducer is zero when the distortion of the deformation, and thus of the polarization, is antisymmetric

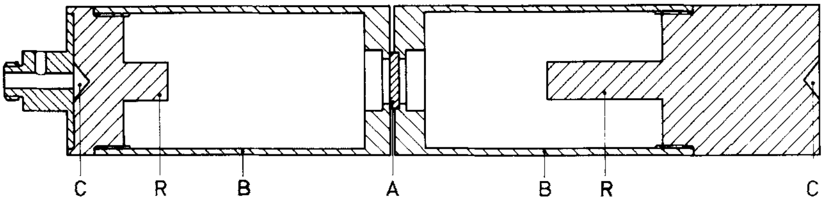

FIGURE 3 Ultrasonic apparatus for sound velocity measurements based on the phase comparison method.

around the center of the crystal, a situation which occurs when the sum of the two echoes vanishes at this central plane.

In both experimental set-up's, standard electronic equipment was used together with a Rockland frequency synthesizer for the generation of the continuous wave.

3 MEASUREMENTS

3.1 Sound velocity

The velocity of sound in toluene and *n*-heptane was measured in the pressure range from 1 to 2634 bar, taking data at intervals of about 202 bar. The measurements on toluene were carried out in the temperature range between 173.2 and 320.3 K and generally with intervals of 25 K at higher temperatures and with intervals of a few degrees at lower temperatures. The measurements on *n*-heptane were carried out in the temperature range between 185.6 and 310.6 K using steps of about 12.5 K. At lower temperatures, the maximum pressure in both cases was limited by the freezing of the liquids.

The acoustic path length, in both cases, was determined by using a comparator with a precision of about 0.01%. In the measurement on toluene by the pulse-echo overlap method, the distance between the crystal transducer and the reflector was 2.0452 cm, at 293.13 K and 1 bar. In the measurement of *n*-heptane, the difference in path length, which determines the sound velocity, was 4.0016 cm, at 294.65 K and 1 bar. The path lengths were corrected for the variation of pressure and temperature using the thermal expansion and the compressibility data of the construction materials. Further, appropriate corrections were introduced in the measured data for both cases to take into account of the effects of diffraction on the transit time, using the method described by Papadakis.[3]

The accuracy of the sound velocity measurements on both the liquids is estimated to be in the order of 0.1 m/s which means that in the full experimental range of pressure and temperature the accuracy is of the order of 0.01%.

3.2 Pressure

The pressure was produced by using a Michels' mercury gas compressor coupled to a hydraulic oil press. The liquid under study was introduced at the gas side of the compressor and on the top of the mercury which acts as a phase separator between the investigated liquid and the oil of the hydraulic system. The pressure was controlled and measured by means of a pressure balance with an accuracy of about 1 in 10^4 over the whole pressure range. Details of the gas compressor and the pressure balance can be found elsewhere.

3.3 Temperature

In each case, the ultrasonic cell was placed inside a steel pressure vessel which formed part of a metal cryostat. Details of the cryostat have been described elsewhere.[4] The temperature of the pressure vessel was maintained constant to within 1 mK by controlling the current through a heating wire wound around the vessel, using a proportional-integral temperature regulation system together with a Thomson bridge. The temperature was measured by means of a calibrated Pt-resistance thermometer with an estimated accuracy of 1 mK. The measurement of temperature consisted of comparing the resistance of the thermometer with a normal resistance of 40 Ω by means of a Diesselhorst potentiometer. The thermometer was calibrated against a standard thermometer of the Van der Waals Laboratory, the KOL 170. All temperatures were measured on IPTS'48 scale.

It was observed during the course of the measurement that the presence of a temperature gradient in the cell has an appreciable influence on the measured sound velocity. The influence was particularly large in the cell used for the velocity measurement on *n*-heptane since this cell can be regarded as a combination of two separate chambers which must be maintained at the same temperature. The temperature gradient over the whole length of the pressure vessel was, therefore, continuously monitored by using a copper-constantan differential thermocouple and reduced to a negligible value by introducing an appropriate amount of heating current to a coil wound around the suspension system of the pressure vessel (cf. ref. 4).

4 EXPERIMENTAL RESULTS

4.1 Sound velocity

The measured values of the sound velocity in toluene and *n*-heptane as a function of pressure and temperature are given in Tables I and II and plotted in Figures 4–7. At each temperature, the experimental data of the sound velocity as a function of pressure can be fitted to the simple expression

$$P = a + bv + cv^3 \qquad (1)$$

in which P is the pressure, v is the sound velocity and a, b and c are coefficients. The values of the coefficients for the two liquids, calculated by means of a least-squares analysis of the experimental results, are given in Tables III and IV. The standard deviations between the experimental and

TABLE I

Velocity of sound in toluene as a function of pressure and temperature.

	velocity of sound in ms^{-1}									
	$T(K)$									
P (bar)	173.18	179.02	182.31	187.12	198.26	223.08	248.11	273.77	298.15	320.30
1.0	1904.8	1874.0	1857.8	1834.1	1778.0	1654.6	1533.7	1414.3	1306.0	1213.4
202.7			1915.4	1892.4	1840.8	1724.1	1611.9	1500.8	1402.3	1318.6
405.3			1968.7	1948.5	1898.5	1788.1	1681.6	1577.4	1486.0	1408.7
608.0				2000.3	1953.1	1847.1	1745.7	1646.9	1560.7	1487.6
810.6					2003.6	1901.9	1804.5	1710.6	1628.2	1558.2
1013.3					2051.1	1953.7	1859.7	1769.4	1690.3	1623.2
1215.9					2096.4	2001.5	1911.1	1823.7	1747.8	1683.3
1418.6					2139.0	2047.1	1959.4	1874.9	1801.1	1739.5
1621.2					2181.6	2091.7	2005.9	1923.6	1851.9	1791.4
1823.9						2132.6	2049.3	1969.3	1899.3	1841.3
2026.5						2172.8	2091.1	2012.9	1945.0	1887.3
2229.2						2211.9	2130.8	2054.5	1988.2	1932.2
2431.8						2248.7	2170.2	2095.2	2030.2	1975.5
2634.5						2284.4	2207.5	2134.0	2070.1	2016.7

TABLE II

Velocity of sound in *n*-heptane as a function of pressure and temperature

	velocity of sound in ms^{-1}									
	$T(K)$									
P (bar)	185.65	198.25	210.35	223.35	236.15	248.65	273.75	285.25	298.15	310.65
1.0	1654.4	1590.5	1533.4	1472.1	1412.5	1356.4	1240.4	1191.2	1136.3	1083.8
202.0		1675.8	1623.0	1567.6	1514.0	1462.9	1360.6	1317.7	1269.9	1224.7
404.7		1752.5	1703.7	1651.8	1602.0	1555.4	1462.1	1422.8	1379.4	1338.6
607.3		1822.4	1776.2	1727.3	1680.8	1637.1	1550.5	1513.9	1473.6	1435.6
810.0		1886.5	1842.6	1796.3	1752.3	1710.9	1629.4	1594.9	1556.8	1521.0
1012.6			1904.0	1859.9	1817.9	1778.6	1701.2	1668.3	1632.9	1597.8
1215.3			1960.6	1919.2	1879.2	1841.1	1767.4	1735.7	1700.9	1668.1
1417.9			2014.5	1974.7	1936.3	1899.7	1828.8	1798.4	1765.0	1733.1
1620.6			2065.6	2027.0	1989.9	1954.8	1886.4	1857.1	1824.3	1793.8
1823.1				2076.6	2041.9	2006.8	1940.6	1912.0	1880.3	1850.5
2025.8				2124.1	2089.3	2056.1	1991.9	1964.2	1933.4	1904.2
2228.4				2169.2	2135.3	2102.8	2040.5	2013.9	1983.7	1955.4
2431.1				2212.7	2179.7	2148.1	2087.4	2060.4	2031.6	2003.7
2633.7				2254.4	2222.1	2191.0	2131.6	2105.6	2077.2	2050.1

TABLE III

Coefficients of expression (1) together with the standard and maximum deviations for toluene at several temperatures

Temp. (K)	a bar	b bar sm^{-1}	$c \times 10^6$ bar s^{3}m^{-3}	stand. dev. ms^{-1}	max. dev. ms^{-1}
198.26	−927.233	−0.759148	0.405268	0.389	0.76
223.08	−878.892	−0.578609	0.405626	0.313	0.57
248.11	−766.529	−0.471259	0.413098	0.290	0.67
273.77	−719.357	−0.323439	0.416343	0.238	0.49
298.15	−644.430	−0.227207	0.422925	0.281	0.52
320.30	−612.156	−0.122582	0.426425	0.453	0.78

fitted values are found to be in the order of the accuracy of the measurements showing the validity of the representation. The maximum deviation from the fitted curve is 0.8 m/s for toluene and 1.7 m/s for *n*-heptane, both occuring at the highest temperature of the present experimental range.

The observed pressure dependence of the sound velocity in toluene agrees reasonably well with the measurements of Hawley *et al.*[5] and Swanson[6] as shown in Figure 4. The present results, however, agree with those of Takagi[7] only up to about 1200 bar. The isobaric plots of sound velocity versus temperature, shown in Figure 5, are not linear but show a distinct curvature at lower temperatures. The curvature, which is always convex towards the temperature axis, is found to be more pronounced at higher pressures. This behaviour differs from the previous work of Nozdrev[8] in which the variation of the sound velocity with temperature at 1 bar was found to be linear. The present value of the sound velocity at 223.15 K and 1 bar is about 2.1% higher than the corresponding value of Nozdrev, while the value at 303.15 K agrees

TABLE IV

Coefficients of expression (1) together with the standard and maximum deviations for *n*-heptane at several temperatures

Temp. (K)	a bar	b bar sm^{-1}	$c \times 10^6$ bar s^3 m^{-3}	stand. dev. ms^{-1}	max. dev. ms^{-1}
210.35	−664.035	−0.391865	0.351135	0.226	0.42
223.35	−696.440	−0.272699	0.344459	0.212	0.41
236.15	−660.719	−0.219373	0.344752	0.323	0.77
248.65	−633.442	−0.168482	0.345800	0.202	0.48
273.75	−556.916	−0.086498	0.348553	0.328	0.68
285.25	−528.715	−0.053274	0.350908	0.422	1.03
298.15	−500.472	−0.015085	0.353472	0.592	1.29
310.65	−476.192	+0.021963	0.356110	0.743	1.69

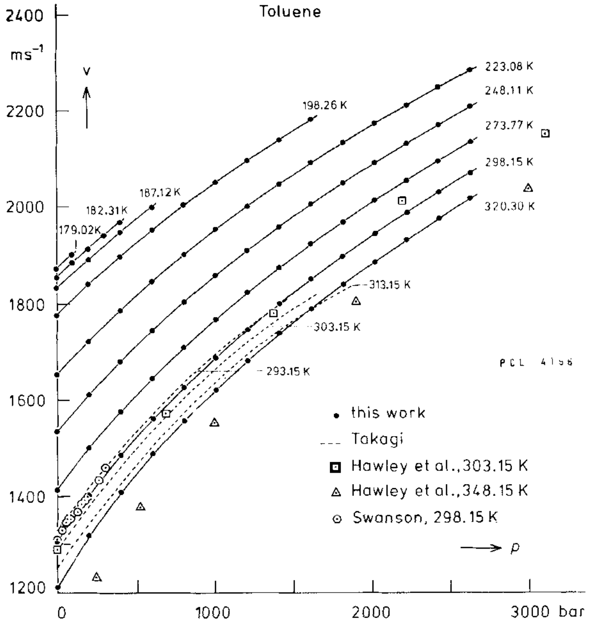

FIGURE 4 The velocity of sound in toluene as a function of pressure.

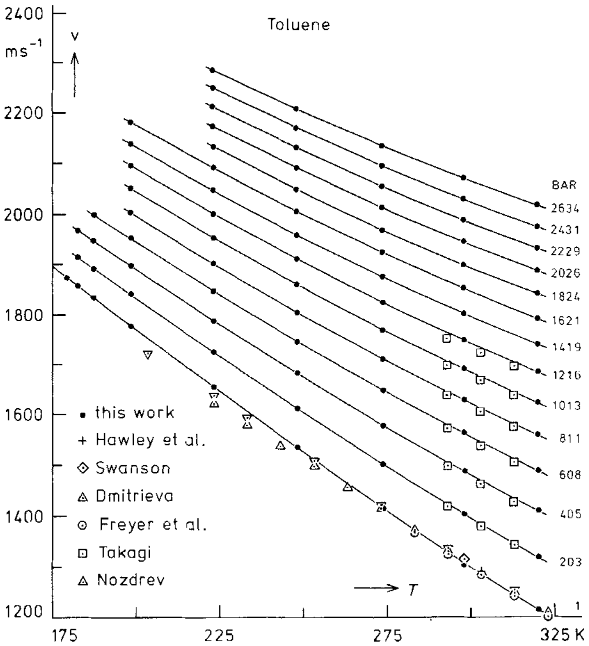

FIGURE 5 The velocity of sound in toluene as a function of temperature.

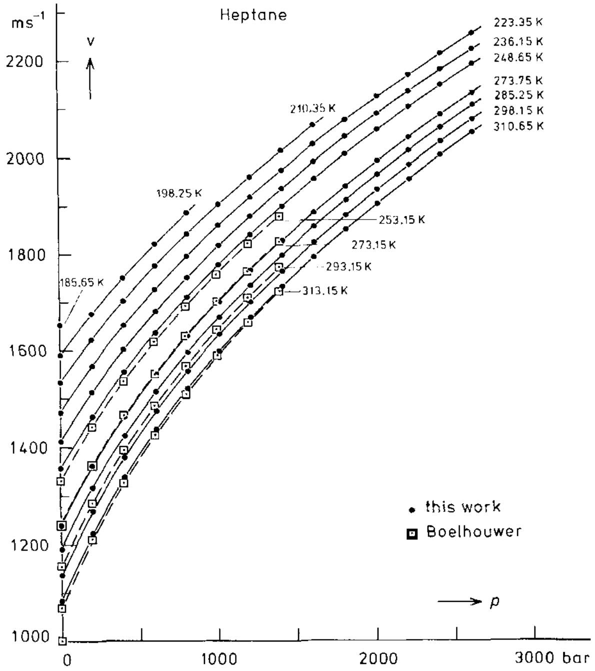

FIGURE 6 The velocity of sound in *n*-heptane as a function of pressure.

well with that of Nozdrev. It may be pointed out here that the non-linear behaviour of the sound velocity versus temperature at lower temperatures was also reported for other organic liquids, e.g. benzene.[7] The present results for toluene at 1 bar differ appreciably from those of Dmitrieva[10] at lower temperatures. Finally as shown in Figures 6 and 7, the present results for *n*-heptane agree well with those measured by Boelhouwer,[11] where the maximum pressure was 1400 bar, and also with those by Freyer[12] and Kireev[13] at 1 bar.

4.2 Density

The density of toluene and *n*-heptane as a function of pressure has been calculated from the measured values of the sound velocity following the method described previously by Davis and Gordon.[14] By a straight-forward integration of the well-known thermodynamic relation

$$\left(\frac{\partial\rho}{\partial P}\right)_T = \left(\frac{\partial\rho}{\partial P}\right)_S + \frac{\alpha^2 T}{C_p} = \frac{1}{v^2} + \frac{\alpha^2 T}{C_p}, \qquad (2)$$

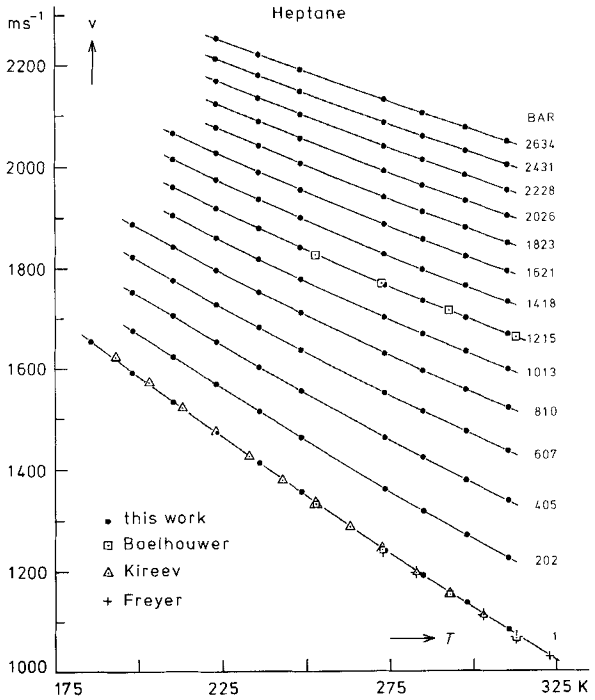

FIGURE 7 The velocity of sound in *n*-heptane as a function of temperature.

with respect to P, one obtains

$$\rho_{P,T} = \rho_{1,T} + \int_1^P \frac{1}{v^2}\,\mathrm{d}P + T\int_1^P \frac{\alpha^2}{C_p}\,\mathrm{d}P, \tag{3}$$

where $\rho_{1,T}$ is the density at 1 bar and T Kelvin, $\rho_{P,T}$ is the density at P and T, α is the volume thermal expansion coefficient and C_p is the specific heat at constant pressure. The integral

$$I = \int_1^P \frac{1}{v^2}\,\mathrm{d}P, \tag{4}$$

has been evaluated by fitting the velocity data with the following polynomial expression:

$$\frac{1}{v^2} = a_0 + a_1 P + a_2 P^2 + \cdots + a_8 P^8 \tag{5}$$

TABLE V

Density of toluene as a function of pressure and temperature

	Density of toluene in kg m^{-3}								
	$T(K)$								
P (bar)	179.020	182.312	187.123	198.263	223.081	248.112	273.768	298.154	320.301
1.01	974.26	971.03	966.34	955.57	931.99	908.62	884.85	862.24	841.49
101.33	978.29	975.13	970.53	960.00	937.03	914.36	891.47	869.83	850.14
202.65		979.12	974.62	964.31	941.88	919.85	897.71	876.92	858.11
303.98		982.98	978.56	968.45	946.52	925.05	903.59	883.52	865.46
405.30		986.71	982.37	972.44	950.97	930.01	909.14	889.71	872.29
506.63			986.05	976.31	955.25	934.75	914.42	895.54	878.69
607.95			989.63	980.04	959.38	939.30	919.45	910.07	884.71
709.28				983.67	963.36	943.67	924.25	906.33	890.42
810.60				987.19	967.21	947.88	928.86	911.34	895.84
911.93				990.61	970.94	951.95	933.30	916.15	901.01
1013.25				993.94	974.56	955.88	937.56	920.76	905.95
1114.58				997.19	978.08	959.68	941.68	925.19	910.69
1215.90				1000.35	981.50	963.38	945.67	929.47	915.25
1317.23				1003.44	984.84	966.90	949.53	933.60	919.64
1418.55				1006.46	988.09	970.45	953.28	937.60	923.87
1519.88				1009.42	991.26	973.85	956.91	941.47	927.97
1621.20				1012.31	994.36	977.16	960.45	945.23	931.94
1722.53					997.38	980.39	963.89	948.88	935.78
1823.85					1000.34	983.54	967.25	952.43	939.52
1925.18					1003.24	986.62	970.52	955.89	943.15
2026.50					1006.08	989.63	973.71	959.26	946.69
2127.83					1008.86	992.58	976.84	962.55	950.14
2229.15					1011.59	995.47	979.89	965.76	953.50
2330.48					1014.27	998.30	982.88	968.90	956.78
2431.80					1016.90	1001.08	985.80	971.97	959.98
2533.13					1019.48	1003.80	988.67	974.97	963.11
2634.45					1022.02	1006.47	991.48	977.91	966.17

The second integral has been evaluated in a similar way as that of Davis and Gordon in which the following thermodynamic relations were used:

$$\left(\frac{\partial \alpha}{\partial P}\right)_T = -\left(\frac{\partial \beta_T}{\partial T}\right)_P \tag{6}$$

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -\left(\frac{T}{\rho}\right)\left[\left(\frac{\partial \alpha}{\partial T}\right)_P + \alpha^2\right], \tag{7}$$

where β_T is the isothermal compressibility at temperature T. By successive integration in (3) starting with known values for the density ρ and the heat capacity C_p at 1 bar, it has been possible to calculate the density ρ as well as several thermodynamic properties such as β_T, α and C_p as a function of

TABLE VI

Density of *n*-heptane as a function of pressure and temperature

	Density of *n*-heptane in kg m^{-3}								
	T(*K*)								
P (bar)	198.250	210.350	223.350	236.150	248.650	273.750	285.250	298.150	310.650
1.01	762.28	752.48	741.91	731.44	721.15	700.22	690.49	679.47	668.66
101.33	767.20	757.79	747.66	737.66	727.87	708.12	699.01	688.74	678.74
202.65	771.89	762.81	753.07	743.47	734.11	715.34	706.72	697.03	687.67
303.98	776.33	767.55	758.15	748.89	739.90	721.95	713.72	704.52	695.65
405.30	780.55	772.04	762.94	753.99	745.31	728.06	720.17	711.36	702.90
506.63	784.58	776.31	767.48	758.80	750.40	733.75	726.15	717.69	709.58
607.95	788.44	780.39	771.80	763.37	755.21	739.10	731.75	723.58	715.78
709.28	792.14	784.29	775.93	767.71	759.78	744.14	737.02	729.11	721.57
810.60	795.70	788.03	779.88	771.87	764.14	748.92	742.00	734.32	727.01
911.93		791.64	783.67	775.84	768.30	753.47	746.73	739.25	732.15
1013.25		795.11	787.32	779.67	772.29	757.81	751.23	743.94	737.03
1114.58		798.47	790.84	783.34	776.13	761.96	755.53	748.42	741.67
1215.90		801.72	794.24	786.89	779.82	765.95	759.66	752.70	746.11
1317.23		804.87	797.53	790.32	783.38	769.79	763.62	756.80	750.36
1418.55		807.93	800.72	793.63	786.82	773.49	767.44	760.75	754.43
1519.88		810.90	803.81	796.85	790.16	777.06	771.12	764.56	758.36
1612.30		813.79	806.82	799.97	793.39	780.52	774.68	768.23	762.15
1722.53			809.74	803.00	796.53	783.86	778.12	771.78	765.80
1823.85			812.59	805.95	799.58	787.11	781.46	775.22	769.33
1925.18			815.37	808.83	802.54	790.26	784.69	778.55	772.76
2026.50			818.08	811.63	805.44	793.33	787.84	781.78	776.08
2127.83			820.72	814.36	808.25	796.32	790.90	784.93	779.31
2229.15			823.30	817.03	811.00	799.23	793.88	787.99	782.45
2330.48			825.83	819.63	813.69	802.07	796.79	790.97	785.50
2431.80			828.30	822.18	816.31	804.84	799.63	793.88	788.48
2533.13			830.72	824.68	818.88	807.54	802.39	796.72	791.38
2634.45			833.10	827.12	821.39	810.19	805.10	799.48	794.21

pressure and temperature. The required density data at 1 bar for the two liquids at various temperatures have been determined from the following 3rd-degree polynomials in T obtained by fitting the experimental data reported in literature:†

$$\text{Toluene:}\quad \rho = 1183.72 - 1.4318T + 1.8779 \times 10^{-3}T^2 - 2.321 \times 10^{-6}T^3 \tag{8}$$

$$\text{Heptane:}\quad \rho = 925.40 - 0.8756T + 0.4567 \times 10^{-3}T^2 - 0.961 \times 10^{-6}T^3 \tag{9}$$

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† API 23-2-(1.101)-d pp. 1-2 (1973).

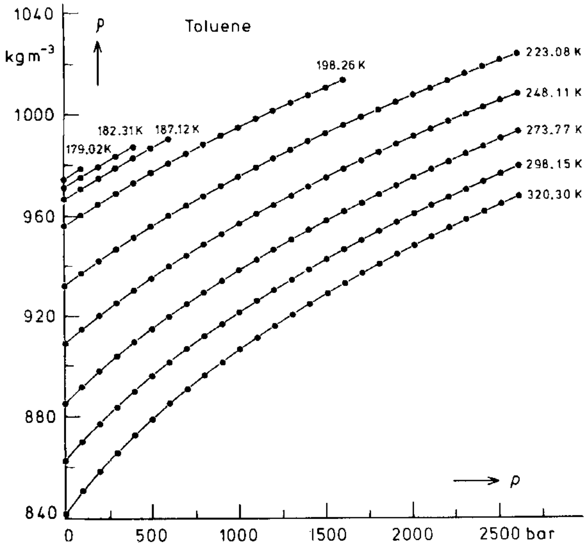

FIGURE 8 The density of toluene as a function of pressure.

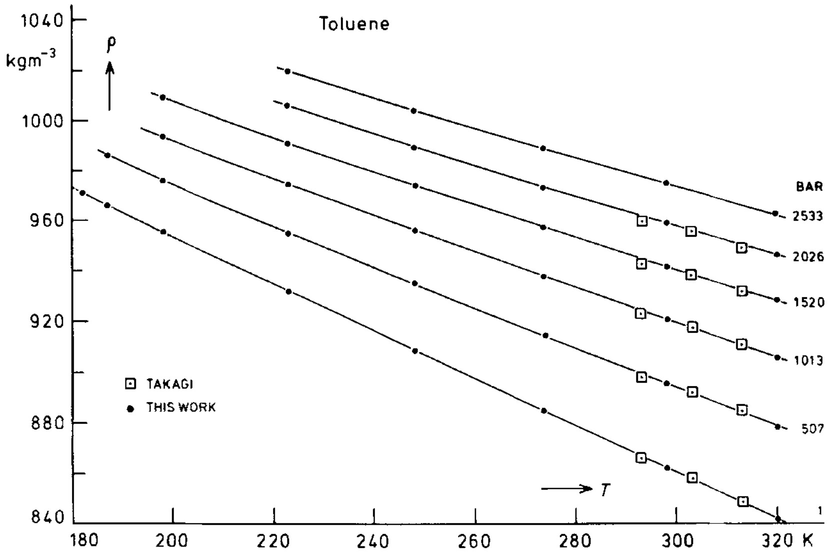

FIGURE 9 The density of toluene as a function of temperature.

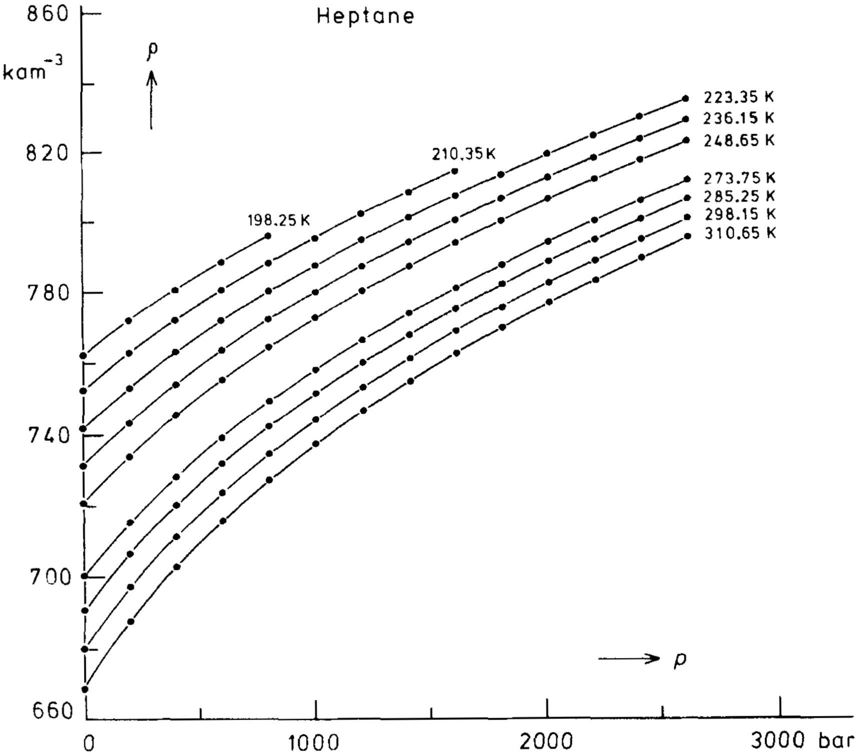

FIGURE 10 The density of *n*-heptane as a function of pressure.

in which ρ is in km . m^{-3} and T in Kelvin. The required specific heat data at 1 bar have been obtained from the following polynomials in T reported previously by Holzhauer:[15]

$$\text{Toluene:}\quad C_p = 2034.50 - 7.92646T + 3.21433 \times 10^{-2}T^2 - 3.11007 \times 10^{-5}T^3 \qquad (10)$$

$$\text{Heptane:}\quad C_p = 8644.59 - 99.4297T + 0.5445218T^2 - 1.3053527\; 10^{-3}T^3 + 1.193352 \times 10^{-6}T^4 \qquad (11)$$

in which Cp is in J/kg.K and T in Kelvin.

The calculated values of the density of toluene and heptane as a function of pressure and temperature are given in Tables V and VI respectively. The P *vs.* ρ isotherms and T *vs.* ρ isobars for toluene are plotted in Figures 8 and 9 respectively while the corresponding plots for *n*-heptane are shown in Figures 10 and 11. As shown in Figure 9, the present results for toluene agree well

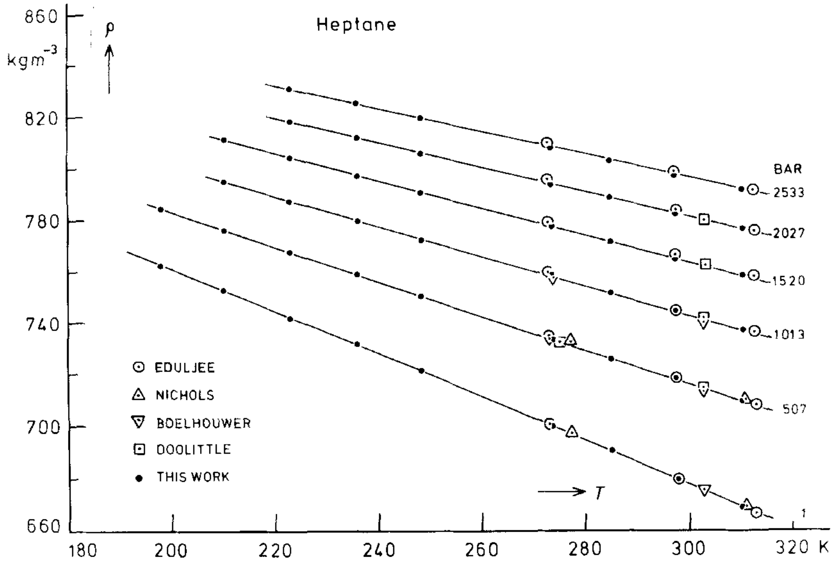

FIGURE 11 The density of *n*-heptane as a function of temperature.

with those reported by Takagi. For instance, at 2027 bar the maximum difference between the present and previous values is found to be about 0.3%. In the case of *n*-heptane, the present density data agree well with those of Eduljee,[16] Doolittle[17] and Boelhouwer.[18] As can be seen in the plotted T *vs.* ρ isobars of Figure 11, the maximum deviation between the present and previous values is about 0.1%. Of course, our data cover a more extensive pressure and temperature range.

TABLE VII

Specific heat ratio (γ) of toluene as a function of pressure and temperature

Temperature (K)	γ_P $P = 1$ bar	γ_P $P = 2634$ bar	Pressure (bar)	γ_T $T = 298.15$ K
173	1.438		1	1.348
179	1.436		405	1.308
182	1.435		811	1.284
187	1.433		1216	1.267
198	1.427		1621	1.254
233	1.409	1.2961	2027	1.243
248	1.388	1.2728	2432	1.234
274	1.366	1.2503	2634	1.231
298	1.348	1.2308		
320	1.335	1.2158		

TABLE VIII

Specific heat ratio (γ) of *n*-heptane as a function of pressure and temperature

Temperature (K)	γ_P $P = 1$ bar	γ_P $P = 2634$ bar	Pressure (bar)	γ_T $T = 298.15$ K
186	1.274		1	1.275
198	1.281		405	1.235
210	1.286		811	1.212
223	1.288	1.180	1216	1.197
236	1.289	1.179	1621	1.186
249	1.289	1.178	2027	1.177
274	1.282	1.174	2432	1.170
285	1.280	1.171	2634	1.167
298	1.275	1.167		
311	1.270	1.162		

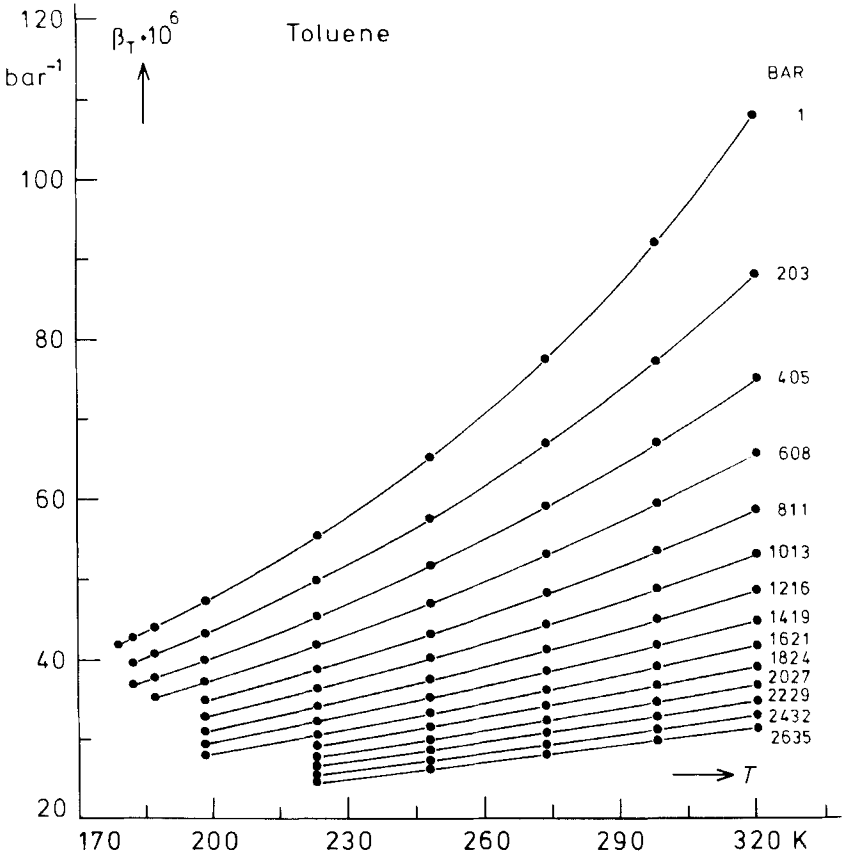

FIGURE 12 The isothermal compressibility of toluene as a function of temperature.

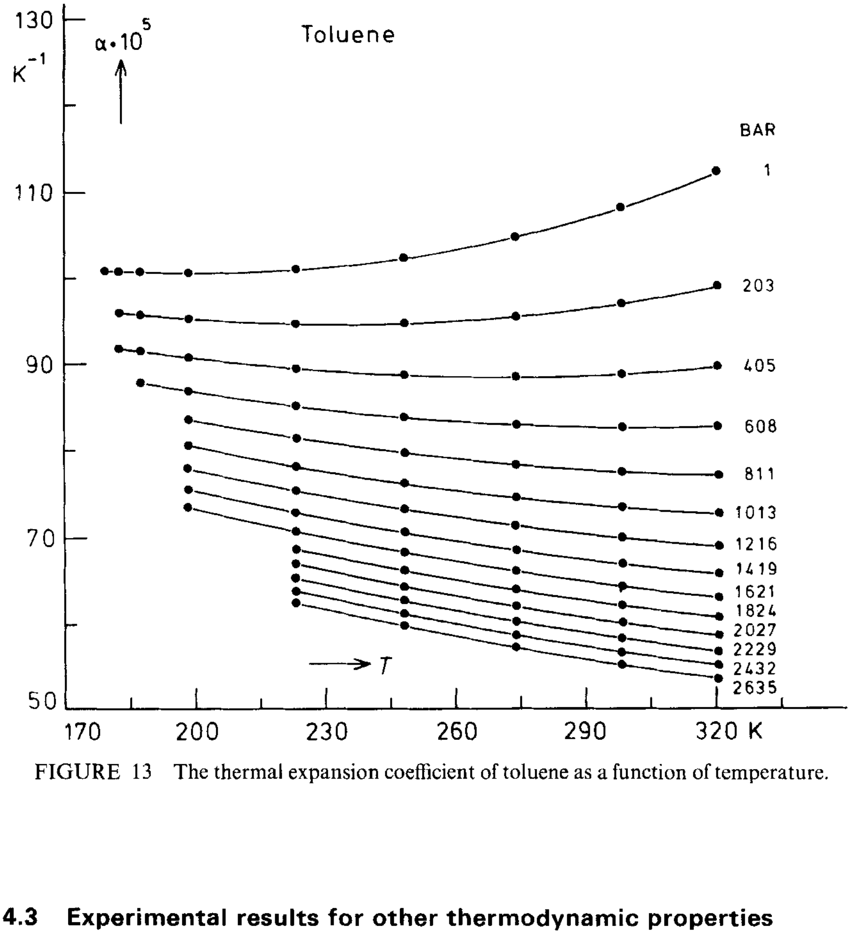

FIGURE 13 The thermal expansion coefficient of toluene as a function of temperature.

4.3 Experimental results for other thermodynamic properties

The calculated values of the isothermal compressibility β_T, *the coefficient of thermal expansion* α and the specific heat at constant pressure C_p as a function of pressure for both liquids are shown in Figures 12–17. In the case of *n*-heptane, the present data of the isothermal compressibility β_T at higher temperatures are compared with those found in literature.[16-20] As shown in Figure 15, in most cases the agreement with previous results is generally good.

The specific heat ratio,

$$\gamma = \frac{C_p}{C_v} = \frac{\beta_T}{\beta_S}, \tag{12}$$

β_S being the adiabatic compressibility, is calculated for both liquids as a func-

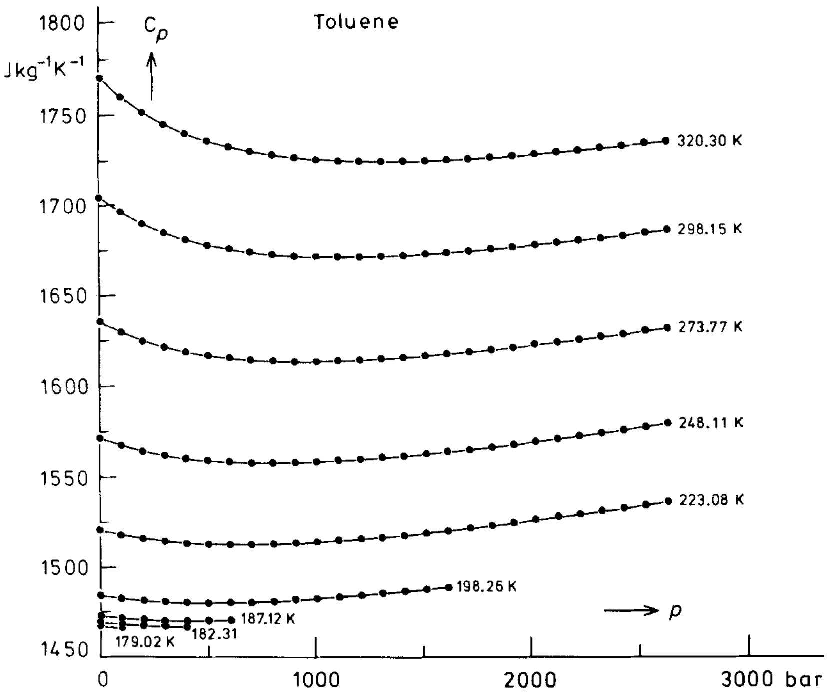

FIGURE 14 The specific heat at constant pressure of toluene as a function of pressures.

tion of pressure at 298.15 K and as a function of temperature at 1 and 2634 bar. The results are given in Tables VII and VIII.

In Figures 18 and 19, the measured sound velocity of the two liquids are plotted as a function of the density and straight lines are drawn through the experimental points of each isotherm. It is clear that the velocity vs. density plots in both cases are very close to linearity and the slope of the lines decreases slowly with increasing temperature.

5 CONCLUSION

Comparing the density data of toluene and *n*-heptane calculated from the present sound velocity data with those obtained from direct measurements by other authors, one may draw the conclusion that the present method is very suitable for precise determination of liquid densities under elevated pressures.

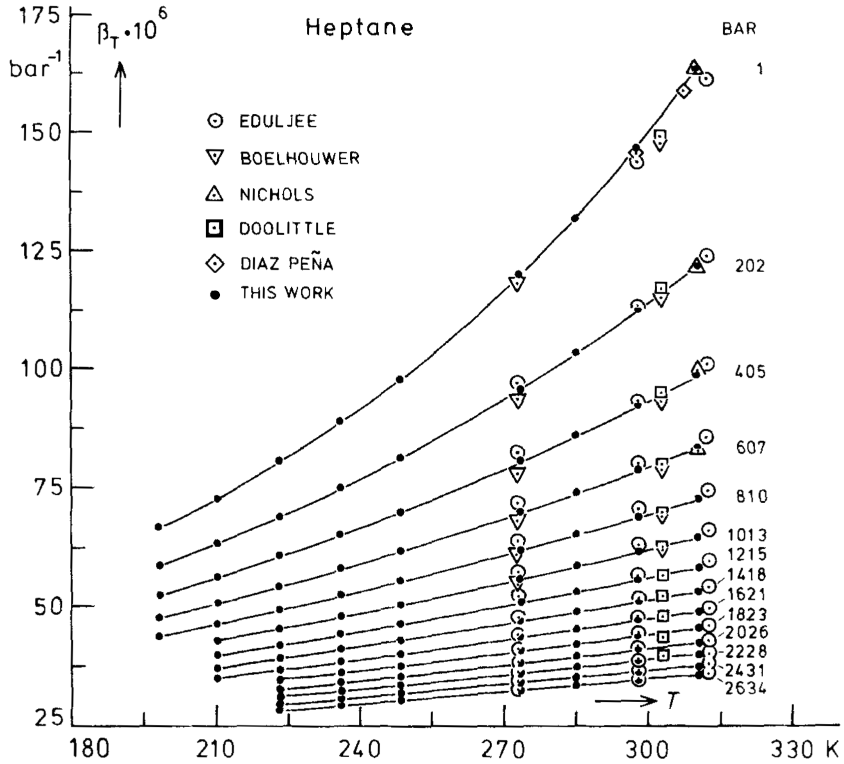

FIGURE 15 The isothermal compressibility of *n*-heptane as a function of temperature.

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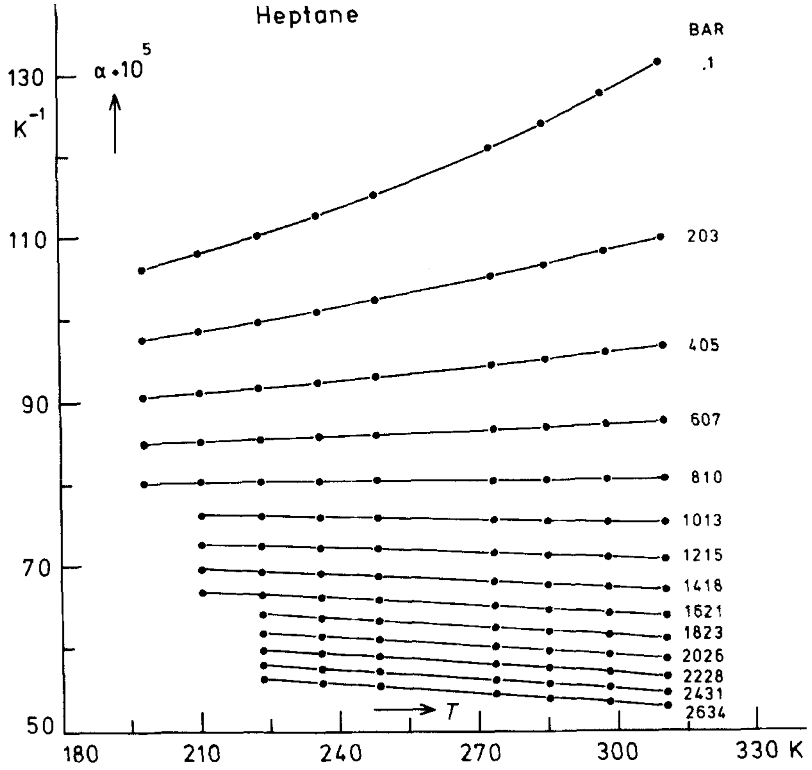

FIGURE 16 The thermal expansion coefficient of *n*-heptane as a function of temperature.

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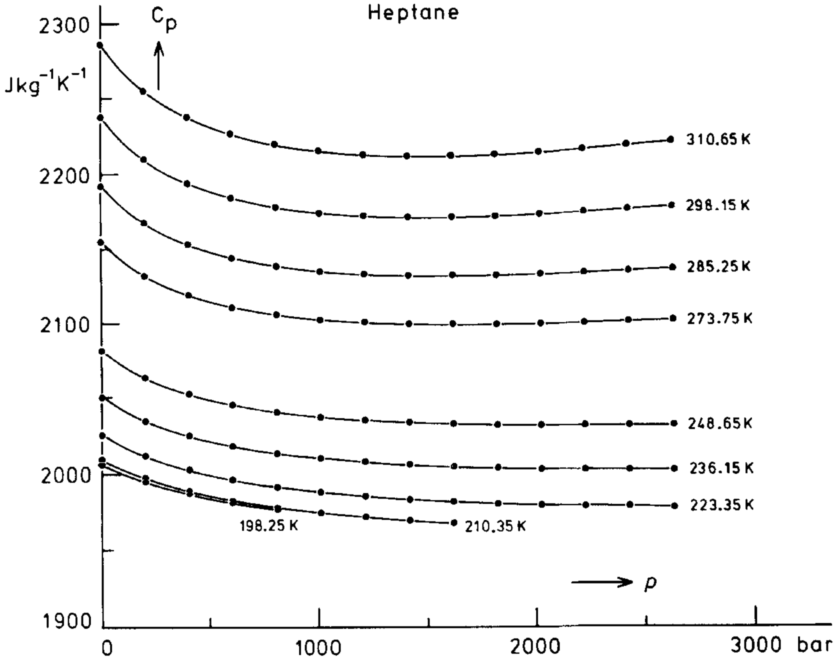

FIGURE 17 The specific heat at constant pressure of *n*-heptane as a function of pressure.

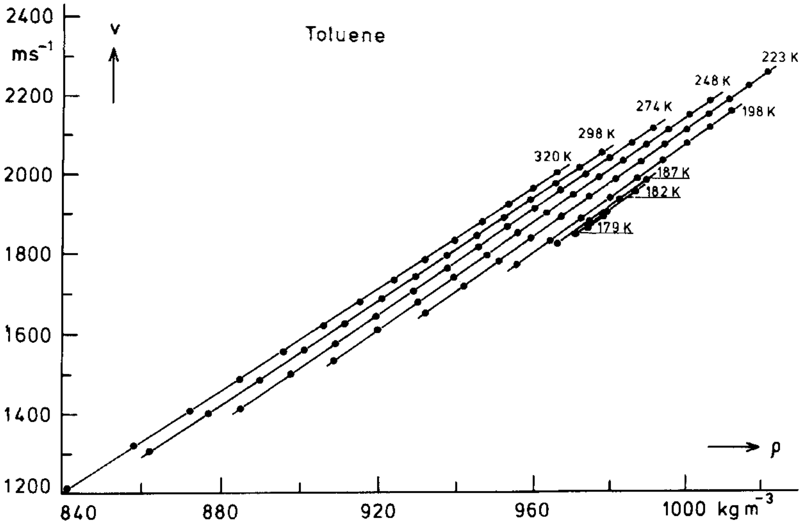

FIGURE 18 The sound velocity in toluene as a function of density.

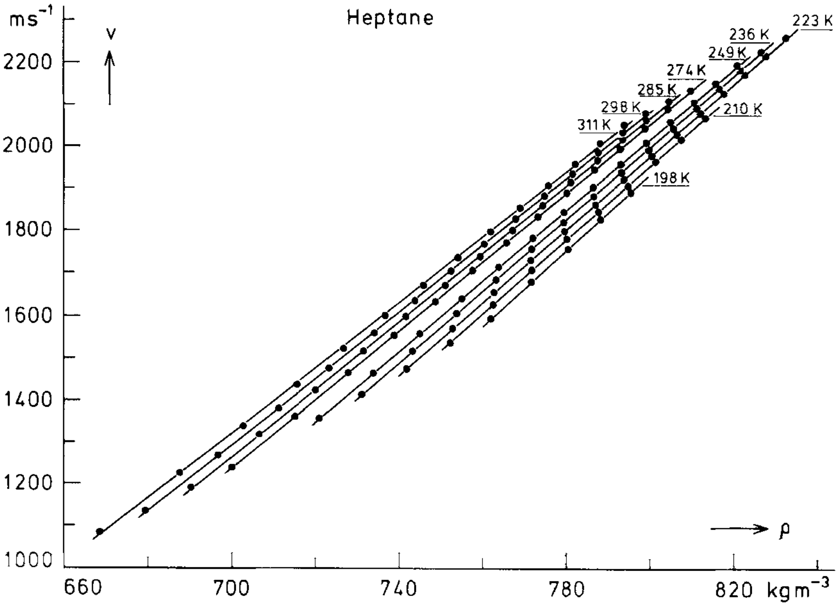

FIGURE 19 The sound velocity in *n*-heptane as a function of density.