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A Vibrating-Wire Densimeter for Liquids at High Pressures: The Density of 2,2,4-Trimethylpentane from 298.15 to 348.15 K and up to 100 MPa

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A new apparatus for the measurement of liquid densities at high pressures is presented. The instrument is a development of a vibrating-wire densimeter described earlier and uses the buoyancy force exerted by the sample fluid on an immersed buoy to alter the tension of a wire from which it is suspended. The tension of the wire is related to its resonant frequency under steady-state transverse vibrations through a rigorous theoretical model which includes a complete analysis of the hydrodynamic effect of the fluid surrounding the wire. The present instrument uses a new design for the measuring cell with the purpose of relieving the degeneracy of perpendicular oscillation modes of the vibrating wire. The modifications lead to a significant increase in the precision of the results. Tests performed on the new apparatus and the operating procedure used, which requires the determination of one cell parameter from one density datum at atmospheric pressure, are described. New results for the density of liquid 2,2,4-trimethylpentane at temperatures from 298.15 to 348.15 K and pressures up to 100 MPa are presented. The data obtained have a precision of $\pm 0.05\%$ at a 2σ level and an estimated accuracy of approximately $\pm 0.1\%$.

KEY WORDS: density; high pressure; isooctane; 2,2,4-trimethylpentane; vibrating-wire densimeter.

1. INTRODUCTION

Many of the currently employed methods of densimetry are not readily adapted to operation over wide ranges of temperature and pressure, so that

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there is a lack of accurate data at high pressures on this fundamental property of fluids.

In many densimeters, such as volumometers [1] and vibrating U-tube densimeters [2], the sample fluid is contained in a volume whose precise determination is the basis for the determination of the density. Such methods suffer from the fact that the prediction of the volume of the containing cell at different conditions of temperature and pressure is difficult. Use of this kind of densimeter thus requires calibration with reference fluids over the whole range of conditions where measurements are to take place and may require calibrants with densities close to that of the fluids to be studied. Except for water and mercury no liquid density is accurately known at elevated pressures, and their particularly low compressibility poses problems to their utilization as reference fluids for such instruments.

Hydrostatic weighing methods [1], on the other hand, determine the density of the fluid through the force exerted on an immersed buoy. The buoy is normally a simple-shaped solid whose properties can be correctly predicted under variable conditions. As a result, these methods may be used in an absolute manner, meaning that there is no need for calibration other than that required for the accurate determination of the volume of the buoy, which can be obtained at normal temperature and pressure. The major problem in applying these methods at very high pressures is the transmission of the buoyancy force through the walls of the pressure vessel to a suitable force balance, and this represents a serious obstacle to most of the magnetic suspension systems used.

In a previous publication [3], a new type of densimeter for measurements in fluids at high pressures was described. The vibrating-wire densimeter makes use of the buoyancy force upon simple-shaped solids, in the same way as hydrostatic weighing densimeters. The buoyancy force sensing device is placed inside the pressure vessel itself and consists of a wire tensioned by the buoy. The tension of the wire is related to its resonant frequency under steady-state transverse vibrations by means of a rigorous theoretical model which includes a complete analysis of the hydrodynamic effects of the fluid surrounding the oscillating wire [4].

The densimeter presented in this work was built using a new cell design. The purpose was to bring the apparatus closer to the theoretical model, relieving the degeneracy of two perpendicular oscillation modes of the wire, thus leading to an improvement in the precision of the results. The operating procedure requires the determination of two cell parameters from one density datum for a reference fluid at atmospheric pressure and the measurement of the resonance frequency under vacuum.

2. PRINCIPLES OF THE METHOD

The basic features of a vibrating-wire densimeter are explained in Ref. 3. The measuring cell comprises a thin metallic wire of radius R and length $2L$ with the top end fixed and a solid cylindrical weight of volume V_w suspended from the lower end. The wire is placed in a uniform permanent magnetic field generated by two rare-earth magnets. An AC current of a specified frequency is passed through the wire, resulting in a force, uniformly distributed along its length, which drives the wire into transverse steady-state vibrations. The wire forms one arm of an AC bridge, so that the velocity amplitude of the oscillations can be detected by electromagnetic induction. The bridge is initially balanced away from resonance, and by sweeping the driving signal through an appropriate frequency range, the resonance curve can be obtained. A diagram representing the bridge circuit and the densimeter cell is presented in Fig. 1.

The presence of the sample fluid contributes to the change in the resonant frequency from the one observed *in vacuo*, mainly through the buoyancy force exerted on the buoy and, to a lesser extent, through the hydrodynamics of the wire motion within the fluid. According to the theory treated in detail in Ref. 4, the condition for velocity resonance of the wire within the fluid is given by the angular frequency ω_r, which is [3] the solution of

$$\frac{\partial}{\partial\tilde{\omega}}\left\{\frac{1}{\tilde{\omega}^2}\left[\left(\tilde{\omega}_B^2-\tilde{\omega}^2\left(1+\frac{\rho}{\rho_s}k\right)\right)^2+\tilde{\omega}^4\left(\frac{\rho}{\rho_s}k'+2\Delta_0\right)^2\right]\right\}=0 \qquad (1)$$

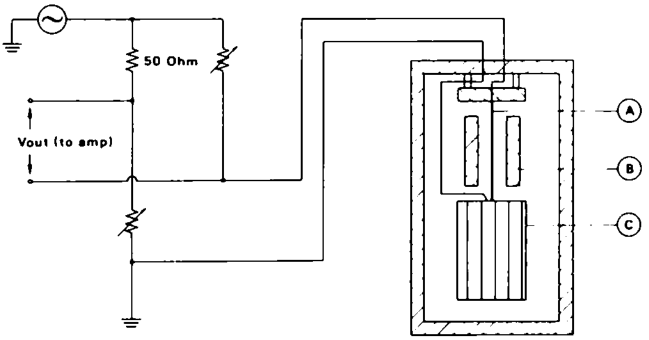

Fig. 1. Diagram of the bridge circuit and of the densimeter cell: (A) vibrating wire; (B) permanent magnets; (C) buoy.

where ρ is the fluid density, ρ_s is the wire density, and k and k' incorporate the hydrodynamic effects of the fluid, being given by

$$k = -1 + 2\,\mathrm{Im}(A) \tag{2}$$

$$k' = 2\,\mathrm{Re}(A) \tag{3}$$

The complex quantity A is related to the modified Bessel functions K_0 and K_1 [5] of the Reynolds number, Ω, by

$$A = i\left\{1 + \frac{2K_1(\sqrt{i\Omega})}{\sqrt{i\Omega}\,K_0(\sqrt{i\Omega})}\right\} \tag{4}$$

Ω being given by

$$\Omega = \frac{\rho\omega R^2}{\eta} \tag{5}$$

where η is the fluid viscosity. The dimensionless frequencies $\bar{\omega}$ are obtained from the angular frequencies by the relation

$$\bar{\omega} = \omega\sqrt{\frac{2\rho_s L^4}{ER^2}} \tag{6}$$

in which E is Young's modulus of the wire material. The quantity Δ_0 in Eq. (1) is the coefficient of internal damping of the wire, which can be determined from the measured ratio of the peak width at half-height, $\omega_+ - \omega_-$, to the resonant frequency *in vacuo*, ω_0, by the equation

$$2\sqrt{3}\,\Delta_0 = \frac{\omega_+ - \omega_-}{\omega_0} \tag{7}$$

The frequency ω_B in Eq. (1) is the resonant frequency of the wire in the hypothetical situation where the wire vibrates *in vacuo* and the buoy is totally immersed in the fluid. Assuming end conditions of the pinned-pinned type for the vibration modes of the wire [6], ω_B can be calculated using the following equation:

$$\omega_B^2 = \omega_0^2 - \frac{\pi g \rho V_w}{4L^2 R^2 \rho_s} \tag{8}$$

where g is the acceleration of gravity and V_w the volume of the buoy. For the same end conditions, the following expression for the resonant frequency of the whole assembly *in vacuo* can be derived:

$$\omega_0^2 = \frac{\pi^2}{4L^2}\left(\frac{gM_w}{\pi R^2 \rho_s} + \frac{\pi^2 R^2 E}{8L^2 \rho_s}\right) \tag{9}$$

where M_w is the mass of the buoy. The first term in parentheses accounts for the tension effect and the second for the elastic behavior of the wire. It should be noted that the reason for assuming pinned-pinned end conditions is one of simplicity. In fact, using the operating procedure described below for our instrument, the results obtained with equations for a wire with clamped ends [4, 6] did not differ significantly.

A set of constraints is imposed by the theory [4], so that a careful design of the instrument is required to satisfy them, as explained in Ref. 3. When these conditions are satisfied, the set of equations presented completely describes the operation of a vibrating wire densimeter, allowing the calculation of fluid densities from measurements of resonant frequencies only, provided that the dimensions of the system, the mechanical properties of the wire, and the viscosity of the fluid are known.

The model provides also a means of obtaining the fluid viscosity from the width of the peak at one half of its height. The two frequencies $\omega_{\pm}$, at which the amplitude is one-half of the amplitude at resonance are given [4] by the solutions of

$$\frac{4}{\tilde{\omega}_r^2}\left[\left(\tilde{\omega}_B^2-\tilde{\omega}_r^2\left(1+\frac{\rho}{\rho_s}k\right)\right)^2+\tilde{\omega}_r^4\left(\frac{\rho}{\rho_s}k'+2\Delta_0\right)^2\right]$$
$$=\frac{1}{\tilde{\omega}_{\pm}^2}\left[\left(\tilde{\omega}_B^2-\tilde{\omega}_{\pm}^2\left(1+\frac{\rho}{\rho_s}k\right)\right)^2+\tilde{\omega}_{\pm}^4\left(\frac{\rho}{\rho_s}k'+2\Delta_0\right)^2\right] \qquad (10)$$

which can be solved numerically for the viscosity through the dependence of k and k' on this property. The precision of the viscosity values obtained by this procedure is determined by the design of the apparatus and also by the lower precision of the measurement of $\omega_{\pm}$ compared to the one attainable with the measurement of the resonant frequency. In the present case the design was directed to optimize the sensitivity to density, not viscosity.

3. THE NEW SUSPENSION SYSTEM FOR THE VIBRATING WIRE

In the first prototype of the measuring cell [3], the vibrating wire was held at both ends by four-jaw chucks, the whole assembly having a cylindrical symmetry. This arrangement causes the two perpendicular modes of oscillation to be nearly degenerate. In fact, two peaks were observed for resonances *in vacuo* at frequencies differing by only about 2 Hz. Rotation of the plane of the magnetic field caused their relative amplitude to be altered until one of them vanished. However, when the same test is performed in a liquid it has been observed that there is always a coupling between the two modes so that the wire precesses about its axis while performing transverse oscillations. This effect not only causes additional energy losses [7] but also leads to a reduction in the precision of the determination of the resonance frequency of either mode.

In the present apparatus, a new mechanical suspension system was developed to relieve the degeneracy between the perpendicular modes, ensuring that the instrument performs in closer accord with the theoretical model of it. The system consists of suspending one end of the wire from a triangular yoke. In this configuration, the apex of the triangle remains a node for oscillations performed in its plane, but not for oscillations perpendicular to that plane, the two perpendicular modes of the assembly's oscillations being substantially separated.

This separation of the natural frequencies of the two modes prevents coupling between them provided that a strict alignment between the plane of the triangle and the plane of the electromagnetic driving force is maintained. Therefore, the supporting triangle must be at the upper end of the wire, firmly aligned with the magnet support, and not associated with the buoy at the lower end of the wire, which has some freedom to rotate. Adopting the triangular yoke support, the two resonant modes of the system could readily be identified and were found to be separated by more than 100 Hz [8].

4. DESCRIPTION OF THE APPARATUS

The source of the driving sinusoidal signal is a function generator with 0.1-mHz frequency resolution and 0.1-mVpp amplitude resolution (Philips PM5191). The input signal is fed into the bridge circuit and its amplitude determined with a 6.5-digit multimeter (Prema 6001, Germany). The out-of-balance signal from the bridge is then fed to a low-noise amplifier specially designed for the purpose and determined with a 6.5 digit multimeter (Keithley 196, USA). The ratio between the output and the input voltages is the primary measured quantity and is proportional to the velocity of the wire oscillation. The use of the ratio in this fashion removes drift in the amplitude of the driving source from consideration. The instruments are controlled from a PC computer through an IEEE-488 bus. The software was designed to perform first a quick search of the peak and then a sweep of a selected frequency interval using a variable-step algorithm, designed to produce faster measurements and to concentrate information in the region near the maximum.

A diagram of the pressure vessel and of the measuring cell is shown in Fig. 2. The densimeter cell consists of an aluminium buoy (G) of about

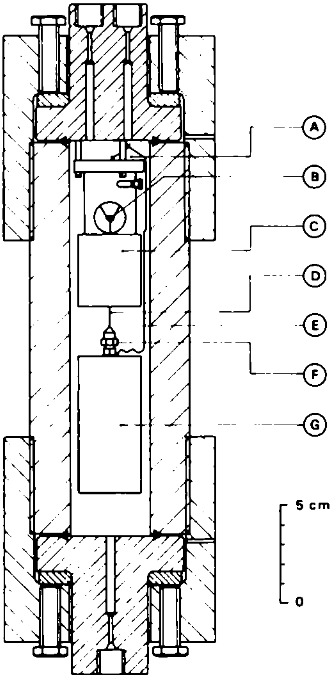

Fig. 2. Densimeter cell with new triangle suspension for the vibrating wire within pressure vessel.

0.150 kg suspended from a tungsten wire (D) 100 μm in diameter and ca. 40 mm in length. Care was taken not to apply a tension to the wire of more than 40% of its yield strength. The upper end of the vibrating wire is clamped by a small stainless-steel piece (B) to two other tungsten wires that form an approximately equilateral triangle with a side length of 15 mm. The upper ends of these two wires are then clamped firmly by two tool-steel bars mounted in the same plate (A) as the magnet support (C). This arrangement allows good alignment between the plane of the triangle and that of the magnetic field. The lower end of the vibrating wire is clamped to the aluminium buoy by a four-jaw stainless-steel chuck (F). A copper wire with a diameter of 8 μm (E) is used to establish electrical contact to the chuck, without disturbing the buoy rest position or significantly altering the wire tension. Owing to the weight of the buoy and to the geometry of the top connection, both ends of the wire act as nodes of the oscillatory motion.

The permanent magnets are two neodymium–iron–boron bars of 30 × 10 × 6-mm size (IBS Magnet, Germany) and generate a field of approximately 0.31 T when separated by 8 mm. They are mounted in an iron case to confine the magnetic field. This case was designed having in mind that the field in the region between the magnets must be uniform, so there should be no iron material in this region.

The cell was mounted inside a cylindrical pressure vessel constructed in nonmagnetic stainless steel, with top and bottom closures using metal-to-metal seals of the "delta-ring" type. There are two high-pressure connections at the top closure, one connected to a vacuum line and the other bearing a two-conductor electrical feed-through. One connection at the bottom closure is used for filling and pressurizing the cell. The entire assembly has a rated working pressure of 100 MPa.

The vessel is supported by a rigid structure equipped with air-damped vibration isolators (Muffelite, UK). It is immersed in a 120-L thermostatic oil bath provided with air bubble dispersers placed at the bottom, to avoid the vibrations caused by motor-driven rotating stirrers. Temperature control is carried out by a PID controller using a thermistor as a sensor and delivering 500 W of heating power. Additional variable heaters can provide a constant background power for operation at higher temperatures. The high-pressure line consists of valves, fittings, and tubing for pressures up to 400 MPa, a pressure relief valve set to 100 MPa, and a piston screw pressure generator for up to 100 MPa (HIP, USA). One capacitance pressure transducer (Setra Systems, USA) protected by a rupture disk, enables readings with an accuracy of ±0.03 MPa up to 35 MPa. One Bourdon manometer (Heise, USA) enables readings with an accuracy of ±0.07 MPa up to 130 MPa. Both manometers were calibrated against a deadweight gauge (Ruska Model 2450, USA). One additional Bourdon gauge (VDO, Germany) is used for monitoring up to 100 MPa. The pressure equipment is mounted inside a protection cabinet, which is itself supported on vibration isolating pads (Muffelite, UK).

Simultaneously with the acquisition of each resonance curve, the temperature is measured by means of a platinum resistance thermometer (Degussa, Germany) placed in thermal contact with the pressure vessel, using a 6.5 digit multimeter (Prema 6001) controlled by the acquisition software. The thermometer was calibrated with a water triple-point cell and against a secondary reference platinum thermometer from 273.15 to 353.15 K. The temperature accuracy is estimated to be ±0.01 K. The typical temperature stability during the acquisition of one density datum is ±0.002 K.

5. OPERATING PROCEDURE

Not all the quantities required in the working equations are easily obtained directly with an accuracy high enough to maintain the overall uncertainty in the determination of densities below ±0.1%. The quantities which can be directly and accurately measured are the resonant frequencies, the wire length, and the buoy mass. The instrument is designed to minimize the hydrodynamic effects and to maximize the sensitivity to the buoyancy force [3].

The quantities whose independent determination is difficult and that may contribute significantly to a loss of accuracy in the measurement are the wire radius, the wire density, and the buoy volume. It is therefore preferable to determine these quantities *in situ* by calibration.

In fact, because the first term in the rhs of Eq. (9) is dominant, a measurement of ω_0 must precisely determine the group $R^2\rho_s$ rather than the independent quantities R^2 and ρ_s. Furthermore, the dominant contribution to the change of resonant frequency of the wire as a result of the buoyancy is determined by this same group, as shown by Eq. (8). Thus the evaluation of R from the group by means of a value for ρ_s is required only to be modestly accurate since it has a relatively minor effect upon the evaluation of the fluid density. Accordingly we have determined the group $R^2\rho_s$ from the resonant frequency of the wire *in vacuo* and then evaluated R by means of a literature value of ρ_s [9]. Finally, the volume of the buoy has been determined from the measurement of the resonant frequency of the wire in a fluid of known density at a single temperature and pressure

Table I. Parameters of the Densimeter Cell

Tungsten wire	
Length (m)	41.48×10^{-3}
Radius (m)[a]	47.596×10^{-6}
Density ($kg \cdot m^{-3}$)	19148.6
Young modulus (GPa)	0.4061
Aluminum weight	
Mass (kg)	0.1549511
Volume (m^3)[b]	54.303×10^{-6}
Resonance in vacuum	
Frequency (Hz)	1280.29
Internal damping coefficient[a]	1.127×10^{-3}

[a] From the resonance curve in vacuum.

[b] From the resonant frequency in 2,2,4-trimethylpentane at 298.15 K and 0.1 MPa, using as a reference the datum for density of 687.85 ± 0.02 $kg \cdot m^{-3}$ obtained by the picnometric method.

through Eqs. (1) and (8). The complete set of parameters for the present instrument is given in Table I.

Naturally, at temperatures and pressures that differ from those of these calibrations, it is necessary to make corrections to the dimensions of the various components. For this purpose, corrections for the effect of temperature changes were made using linear expansion coefficients for tungsten and for aluminium, as described in Ref. 4. No corrections were made for the effect of pressure, as they turn out to be insignificant in the experimental range covered in this work.

Table II. Density of 2,2,4-Trimethylpentane

Temperature (K)	Pressure (MPa)	Res. freq. (Hz)	Density (kg · m^{-3})
298.15	0.10	1086.69	687.85
	10.20	1083.48	697.87
	20.25	1079.90	707.03
	30.00	1077.06	714.65
	40.15	1074.15	722.30
	50.15	1071.55	728.85
	60.15	1069.08	734.90
	70.10	1066.83	740.08
	80.10	1064.54	745.36
	90.15	1062.27	750.48
	100.10	1060.10	755.20
323.15	0.10	1093.79	666.82
	10.25	1089.78	678.84
	20.15	1086.39	688.68
	30.20	1083.17	697.84
	40.10	1080.31	705.69
	50.25	1077.60	712.94
	60.10	1075.10	719.44
	70.10	1072.68	725.60
	80.10	1070.36	731.39
	90.15	1068.07	737.00
	100.10	1065.96	742.00
348.15	0.10	1100.86	644.64
	10.10	1096.39	658.57
	20.10	1092.52	670.34
	30.20	1089.05	680.58
	40.25	1086.00	689.37
	50.15	1083.21	697.29
	60.10	1080.57	704.43
	70.10	1078.00	711.42
	80.15	1075.58	717.88
	90.10	1073.22	724.05
	100.10	1070.98	729.80

Measurements were performed on 2,2,4-trimethylpentane, which is a recommended reference material for the determination of liquid densities at atmospheric pressure and at temperatures between 293.15 and 323.15 K [10]. Previous measurements at high pressures were found in the literature: up to 500 MPa at temperatures from 298.15 to 398.15 K at 25 K intervals [11] and up to 280 MPa in the temperature range from 278.15 to 338.15 K [12]. These two sets of data were obtained using bellows volumometers and have stated accuracies of the order of ±0.1%. In the latter work, however, only correlating equations are published but the direct experimental data are not presented.

Our sample of 2,2,4-trimethylpentane was obtain from Merck, p.a. grade, with a stated purity of 99.5%. It was dried over 4-Å molecular sieves and distilled over calcium hydride before use. The initial purity was confirmed and the final purity of 99.8% was checked by gas chromatography. The density of the sample at atmospheric pressure and 298.15 K was measured independently, using an Ostwald glass pycnometer as mentioned in Ref. 13, and a reference value of $687.85 \pm 0.02\ \mathrm{kg \cdot m^{-3}}$ was obtained. This is in total agreement with the IUPAC recommended value and also with the values of Refs. [11, 12] obtained at atmospheric pressure with vibrating-tube densimeters. To check for any loss of purity in the sample, the resonant frequency at 0.1 MPa and 298.15 K was verified at the end of the measurements. The density was again checked with a vibrating-tube densimeter for confirmation.

6. RESULTS AND DISCUSSION

Measurements of the density of 2,2,4-trimethylpentane were performed along three isotherms of 298.15, 323.15, and 348.15 K at pressures from 0.1 to 100 MPa. Some resonance curves are shown in Fig. 3. The values for the viscosity were taken from Ref. 14. They were obtained for the same isotherms with a falling-body apparatus and have an estimated accuracy of ±2%. Interpolation of viscosity with pressure was performed using a Tait-type equation given in Ref. 14. The deviations of the temperature from a nominal isotherm temperature was always less than ±0.01 K. The density results are listed in Table II and graphically presented in Fig. 4.

Along each isotherm, about one half of the data were obtained during the pressurization cycle and the other half during depressurization. These two sets of data were entirely consistent. The typical reproducibility of the resonant frequency under any specified conditions was ±0.025 Hz, which corresponds to a precision of about ±0.03% in the density. The precision of the present data is estimated as better than ±0.05% at a 2σ confidence level. The accuracy of our results can be estimated as ±0.1%, owing mostly

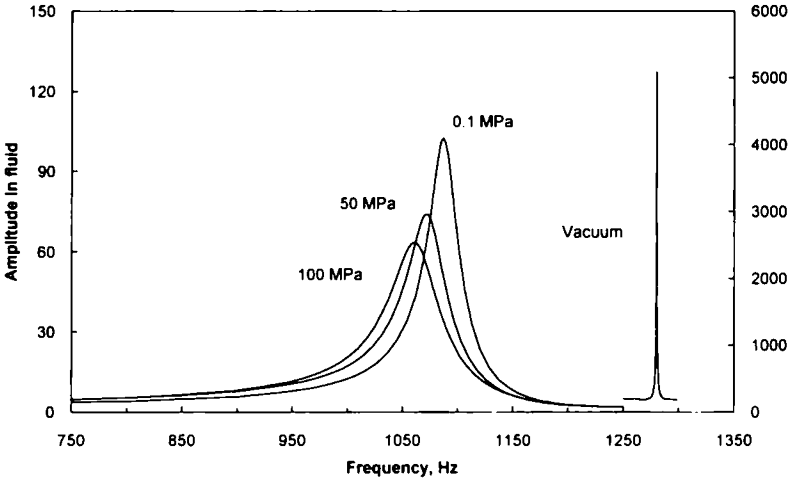

Fig. 3. Resonance peaks in 2,2,4-trimethylpentane at 298.15 K.

to the precision of the available literature data and to the uncertainties in the viscosity data necessary for the calculation of density in the present measurements.

A correlation of the bulk modulus type was found to represent the pressure dependence of the present data. The secant bulk modulus, K, is calculated from the density data by

$$K = \rho \frac{p - p_0}{\rho - \rho_0} \qquad (11)$$

where the subscript 0 refers to atmospheric pressure in the present case. Then the parameters K_0, a, and b are obtained by least-squares fitting of the equation

$$K = K_0 + a(p - p_0) + b(p - p_0)^2 \qquad (12)$$

Table III. Parameters of Eq. (12)

T(K)	K_0(MPa)	a	b (GPa^{-1})	σ (%)
298.15	520.63	5.497	−8.450	0.03
323.15	419.15	5.360	−9.869	0.02
348.15	729.41	7.537	−14.22	0.02

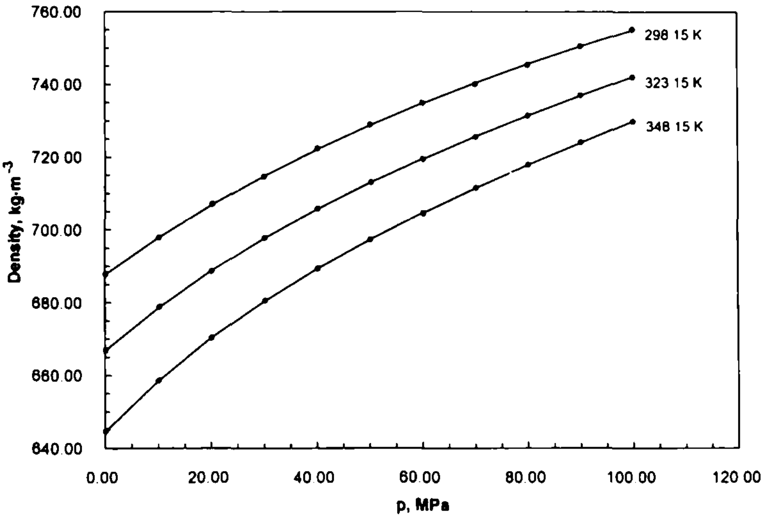

Fig. 4. Density data of 2,2,4-trimethylpentane.

Interpolation with density is the made using

$$\rho_{\text{corr}} = \rho_0 \frac{K}{K-(p-p_0)} \tag{13}$$

The values of the parameters of Eq. (12) for the three isotherms, together with the standard deviations for the density estimation, are presented in Table III. The overall standard deviation is smaller than ±0.03%. Deviations of the present data from the correlation as well as those of the results of Dymond et al. [11] and of the correlations of Malhotra and Woolf [12] are presented in Fig. 5.

The agreement with the results of Ref. 11 is very good at pressures above 50 MPa, only one point deviating by more than ±0.1% from the correlation of the present data. That single datum in fact deviates by 0.2% from the original correlation of the data given in Ref. 11. At lower pressures the results reported in Ref. 11 have a worse precision owing to the fact that, in the bellows volumometer employed, the displacement of the bellows at low pressures is small and therefore more difficult to determine. This partly explains the value of the deviations seen in Fig. 5.

The correlations published by Malhotra and Woolf [12] show a good agreement with the present data and the data in Ref. 11 at 298.15 K, but at 323.15 K, which is their highest temperature, the deviations increase significantly with pressure, reaching almost 0.3% at 100 MPa.

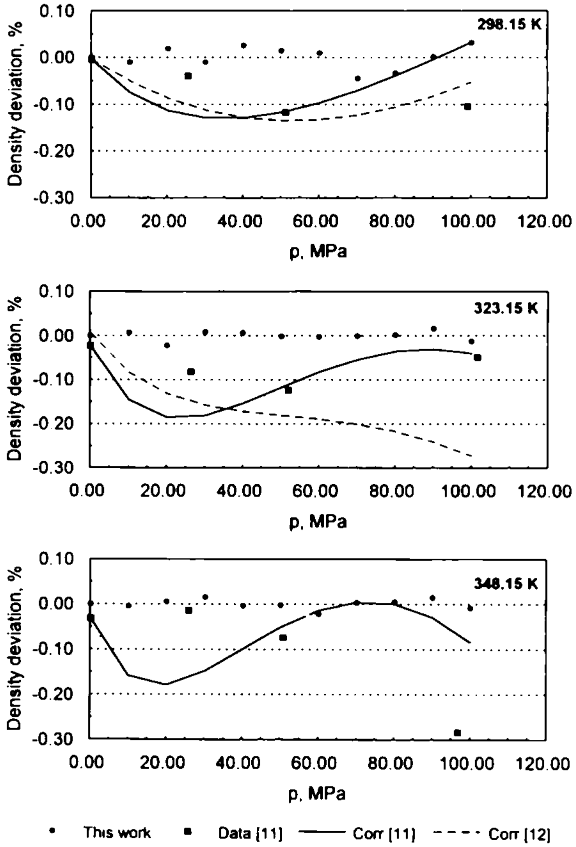

Fig. 5. Deviation plots of density data from our correlation curves.

7. CONCLUSIONS

A vibrating-wire densimeter has been constructed which employs a new type of suspension mechanism for the vibrating wire. The new arrangement has increased the precision of the measurements and the existence of a rigorous mathematical model describing the behavior of the vibrating wire allows the instrument to produce accurate measurement of density over wide ranges of pressure and temperature. Calibration of the instrument requires the determination of just two cell parameters from one density datum and a measurement *in vacuo*. The density of 2,2,4-trimethylpentane was measured at 298.15, 323.15, and 348.15 K and up to 100 MPa, the results having a precision better than ±0.05% at a 2σ confidence level and an accuracy that can be estimated as ±0.1%.

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