International Journal of Thermophysics, Vol. 12, No. 2, 1991

A Vibrating-Wire Densimeter for Measurements in Fluids at High Pressures

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Received April 5, 1990

The paper describes a new type of densimeter especially designed for the accurate measurement of fluid densities at pressures up to 400 MPa. The densimeter makes use of the buoyancy force exerted on a mass immersed in the test fluid to alter the resonant frequency of a thin wire from which the mass is suspended. The resonant frequency of the wire carrying the mass is related to the fluid density by means of working equations which are based on a complete analysis of the fluid motion around the wire. Preliminary results are presented for *n*-octane at pressures up to about 100 MPa near ambient temperature. The results show that the instrument has a precision of ±0.1 % in density at elevated pressures when evaluated on a relative basis, while the accuracy is estimated to be one of ±0.2 %.

KEY WORDS: densimeter; density; resonance; vibrating-wire instrument.

1. INTRODUCTION

It has proved rather difficult to measure the density of fluids over a range of pressures beyond 40 MPa with an accuracy comparable with that attainable at atmospheric pressure. Only for relatively incompressible fluids such as mercury and water have such measurements been possible. Since the fluid density is a prime variable in the description of the behaviour of other fluid properties [1], the lack of density data inhibits an interpretation of many other measurements.

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0195-928X/91/0300-0357$06.50/0

The predominant reason for the lack of accurate density data at elevated pressures derives from the fact that in most densimeters the test fluid is contained within a sample volume whose magnitude is both vital to the measurement and dependent on pressure in a manner not always readily predicted or reproducible. The fluid densimeter described in this work, therefore, makes use of a different principle in which the test fluid surrounds the important elements whose dimensions enter into the evaluation of the fluid density. Furthermore, all of these elements are solids of simple shapes so that the small effects of high, hydrostatic pressures are readily calculated. The densimeter is therefore an extension of an earlier study [2, 3] carried out to secure an improved sensitivity and precision.

2. EXPERIMENTAL

2.1. Principle of the Method

Figure 1 shows a schematic diagram of the vibrating-wire densimeter. The densimeter consists of a solid weight, W, of volume V_w, and a thin metallic wire, S. The wire carries the weight at a lower end and is fixed at an upper end. The wire has a length, $2L$, and forms part of an electrical circuit through which a variable frequency alternating current is supplied. The wire is mounted in a uniform magnetic field so that it is forced to unergo steady-state transverse vibrations *in vacuo* or in a fluid.

The presence of the fluid changes the resonant frequency of the transverse vibrations of the wire largely through the effect of buoyancy on the

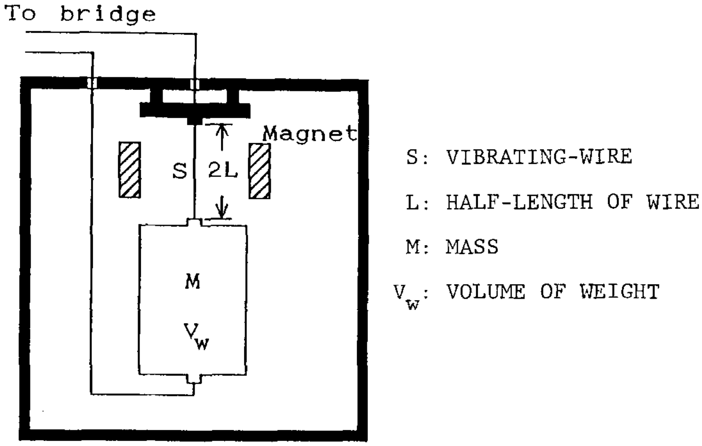

Fig. 1. A schematic diagram of the densimeter cell.

weight and, to a lesser extent, through the hydrodynamic effects associated with the motion of the wire. The resonant frequency of the wire in transverse vibrations can, therefore, be used for determining the fluid density. The difference between this densimeter and that described earlier [2, 3] therefore consists of an enhancement of its sensitivity by making use of the buoyancy effect of the fluid upon the weight.

2.2. Working Equations

The theory of an instrument in accord with this principle has been treated in detail elsewhere [2]. However, that study provides only one part of the complete theory of the instrument to be described here since it is concerned only with the effect of the fluid flow around the wire on its resonant frequency. It is now also necessary to consider the effect of the fluid density on the buoyancy of the suspended weight which acts to reduce the tension on the wire and thereby reduce its resonant frequency. The inclusion of this second effect is a trivial addition to the earlier theory [2]. Consequently, the resonant frequency of the wire, ω_r, defined in terms of the maximum velocity observed for the wire vibrating in the fluid is given by the solution of the equation

$$\frac{d}{d\omega}\left\{\frac{1}{\omega^2}\left[(\omega_b^2-\omega^2(1+(\rho/\rho_s)k)^2)+\omega^4[(\rho/\rho_s)k'+2\Delta_0]^2\right]\right\}=0 \quad (1)$$

where

$$\omega_b^2=\omega_0^2-\pi\rho g V_w/(4L^2R^2\rho_s) \quad (2)$$

Here ρ represents the fluid density and ω the angular frequency of forced vibrations of the wire and ω_0 is the resonant frequency of the wire *in vacuo*. In addition, R is the radius of the vibrating wire, L its half-length, and ρ_s its density. The symbol Δ_0 represents the logarithmic decrement of the oscillations of the wire *in vacuo* and can be related to the width of the resonance curve under the same conditions, $\Delta\omega_0$, by the equation

$$\frac{\Delta\omega_0}{\omega_0}=2\sqrt{3}\,\Delta_0 \quad (3)$$

for $\Delta_0 \ll 1$.

The angular frequency ω_b of Eq. (2) represents that resonant frequency that arises from the effects of buoyancy alone on a weight of volume V_w in the presence of a gravitational acceleration, g.

The two remaining quantities of significance in Eq. (1) are k and k'.

They contain the hydrodynamic effects on the motion of the wire vibrating in the fluid and are given by the equations, [2]

$$k = -1 + 2\,\mathrm{Im}(A) \tag{4}$$

$$k' = 2\,\mathrm{Re}(A) \tag{5}$$

with

$$A = i\left\{1 + \frac{2K_1([i\Omega]^{1/2})}{[i\Omega]^{1/2}\,K_0([i\Omega]^{1/2})}\right\} \tag{6}$$

in which

$$\Omega = \rho\omega R^2/\eta \tag{7}$$

In Eq. (6), K_0 and K_1 are modified Bessel functions and the dimensionless quantity, Ω, defined in Eq. (7) is the Reynolds number for the motion of the wire in the fluid of viscosity, η.

It is important to emphasize that Eqs. (4) to (6) are valid only under a set of constraints determined by Retsina et al. [2]. Specifically, these constraints are

$$L/R \gg 1 \tag{8}$$

$$\frac{\omega\varepsilon R}{c} \ll 1 \tag{9}$$

$$\varepsilon \ll \Omega \ll 1/\varepsilon^2 \tag{10}$$

in which εR is the amplitude of the wire motion and c is the speed of sound in the fluid. In addition, it is presumed that the wire vibrates in a fluid whose outer boundary, radius R_c, is placed at an infinite distance from the wire. It is shown later that it is possible to design and build an instrument to satisfy all of these constraints except that placed on the radius of the outer boundary of the fluid. However, an appropriate analysis demonstrates that even this effect can be rendered very small in a practical instrument and that a correction for it can be applied [2].

Provided that the volume of the suspended weight, V_w, the density of the vibrating wire, ρ_s, and its radius, R, and half-length, L, are known, it is possible to make absolute determinations of the fluid density, ρ, using measurements of the resonant frequency of the wire in the fluid, ω_r, and that *in vacuo*, ω_0, the logarithmic decrement *in vacuo*, Δ_0, and the fluid viscosity, η. Naturally, if it is desired to operate the instrument over a range of pressures and temperatures, it is necessary to account for dimensional changes in the solid elements of the instrument. However, the design and construction of the instrument can be made such as to make these effects small and easily calculable.

3. THE INSTRUMENT

3.1. Design Features

Figure 2 shows the vibrating-wire densimeter designed and constructed during the present study for measurements of the density of liquids at high pressures up to 500 MPa. The weight, 1, is manufactured from aluminium and is suspended from a tungsten wire, 2, of nominal radius 50 μm and nominal length 44 mm. Thus $(L/R) \simeq 900$ and the condition given by Eq. (8) required by the theory is adequately satisfied. The wire is

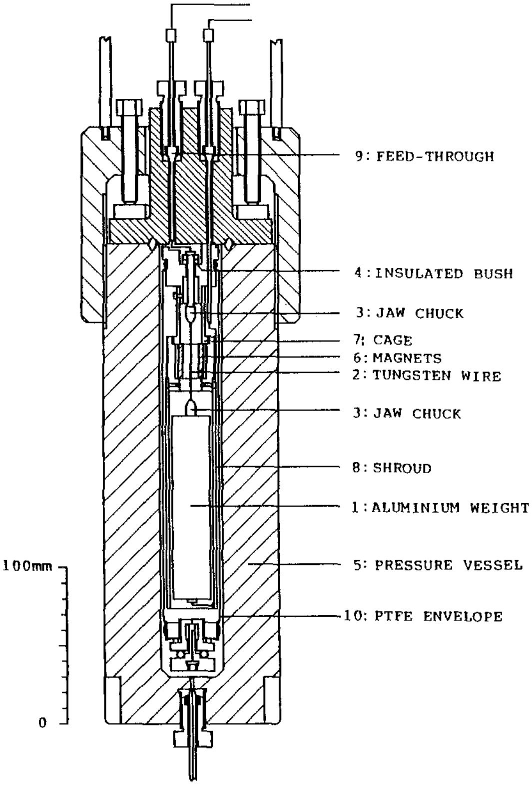

Fig. 2. The densimeter and the high-pressure vessel.

clamped at each end in a four-jaw chuck, 3. The upper chuck is held in an electrically insulating bush, 4, from a top plate supported from the upper closure of the pressure vessel, 5. Two ceramic magnets (Sm–Co alloy), providing a magnetic flux density of 0.2 T, are supported in a cage, 7, that can be rotated around the axis of the instrument containing the wire in order to secure optimal alignment. The lower part of the housing is completed by a stainless-steel shroud, 8. The electrical drive for the wire is passed into the high-pressure system through a feed-through, 9, then passed through the upper chuck, and finally, returns through a loosely-coiled connection at the bottom of the weight and the shroud, 8. The test fluid is confined within a thin-walled cylindrical PTFE envelope, 10, sealed to the pressure vessel cap and closed at its lower end. The envelope is placed within the pressure vessel to which hydraulic pressure can be applied in order to pressurise the test fluid in the PTFE sleeve. Pressures up to 400 MPa may be generated in this way.

The entire pressure vessel is suspended on a vibration-free support in a thermostated oil bath as shown in Fig. 3. The bath maintains the temperature within ±20 mK over a period of hours for the temperatures up to 363 K that are currently attainable. An oil-filled hand pump is used to generate hydraulic pressures in the pressure system that are measured with calibrated Bourdon-type pressure gauges with an accuracy of ±0.5 MPa.

The densimeter described above allows electrical measurements of the resonant frequency of the wire carrying the weight for transverse vibrations

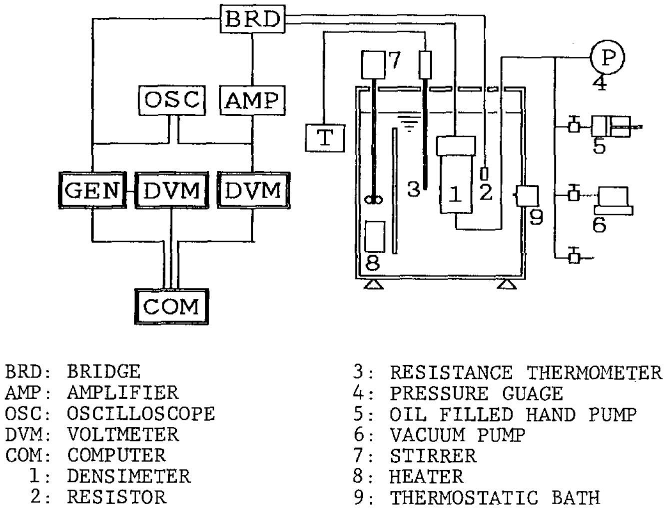

Fig. 3. A block diagram of the complete densimeter.

of the fundamental mode both *in vacuo* and in the fluid. The measurements are achieved with a bridge circuit in which the off-resonance impedance of the wire is compensated by a dummy resistor so that it becomes possible to separate the signal induced in the wire as a result of its motion in the uniform magnetic field from the signal used to drive its motion. The driving signal is provided by a computer-controlled frequency generator programmed to step the driving frequency in increments of as little as 0.01 Hz through the resonant frequency. At each frequency the driving voltage and the rms value of the induced signal are measured simultaneously, and the ratio formed as a measure of the velocity response of the vibrating wire. The simultaneous measurement of the driving voltage and the response eliminates any deleterious effects from drive voltage drift. Again, the control and logging of all electrical measurements are under the action of a personal computer through an appropriate interface.

The magnitude of the induced signal in the wire provides the information necessary to evaluate the amplitude of the motion of the wire, εR, and hence to ensure that the conditions (9) and (10) required by the theory are satisfied. In all the experiments reported here this proved to be the case.

Typical resonance curves measured at two different pressures and at a temperature 298.83 K for *n*-octane are shown in Fig. 4, together with a resonant peak *in vacuo* at the same temperature. It can be seen that the presence of the fluid changes the resonance characteristics, the resonant frequency in the fluid, ω_r, decreases by about 200 Hz, owing principally to the increasing density of the fluid, and the width of the peak, $\Delta\omega_r$, increases, mainly because of the increase in the fluid viscosity.

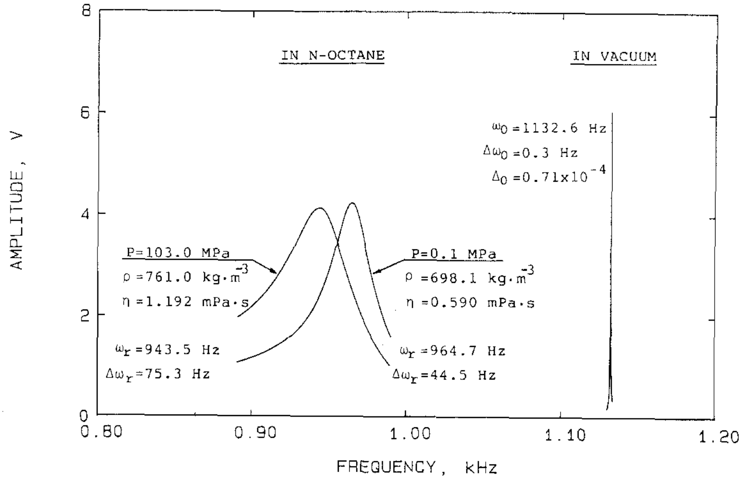

Fig. 4. The resonant curves for the wire *in vacuo* and in *n*-octane.

The definition of the resonance condition contained in Eq. (1) corresponds to a maximum in the rms signal induced in the vibrating wire. Thus, in principle, it is sufficient to observe the peak value in the recorded signal to determine the resonant frequency, ω_r. This direct measurement yields a precision of ±0.2 Hz in the resonant frequency in a liquid with the present configuration. An enhanced precision of ±0.1 Hz can be attained by interpolating with a suitable functional form within the recorded points near the resonance maximum. In the case of measurements *in vacuo*, the sharpness of the resonance curve means that an even higher precision can be obtained in ω_0—generally of the order of ±0.02 Hz. Under the same conditions Δ_0 can be determined from the observed width of the resonance curve according to Eq. (3). Because $\Delta \gg \Delta_0 \sim 10^{-5}$, the precision of this measurement need not be high and it is therefore straightforward to perform it with sufficient accuracy.

3.2. Measurement Procedure

As indicated earlier, it is possible to perform absolute density measurements on fluids with this instrument if the physical properties and dimensions of various elements of the instrument are known with sufficient precision. In practice, this is seldom likely to be possible, nor, indeed, is it an efficient process compared with the performance of relative measurements, provided that any calibration can be performed under conditions where the density of one or more fluids is known accurately. In the case of the particular instrument described here, it has not proved possible to find a means of measuring the radius of the tungsten wire with the precision of better than ±0.02 μm which is necessary to secure absolute density measurements accurate to ±0.1%. Equally, the densities of tungsten reported in the literature [4] show substantial variations among various authors' results; moreover, it is likely that none of these values is appropriate to the actual samples of material employed in this work. Consequently, it is preferable to operate the instrument in a relative manner to determine those quantities which cannot be obtained directly.

The mass of the weight and the chuck assembly, M_w, can obviously be determined by direct weighing. The frequency of the wire *in vacuo* is given by

$$\omega_0^2 = \frac{\pi^2}{4L^2}\left\{\frac{M_w g}{\rho_s \pi R^2} + \frac{R^2 E \pi^2}{8L^2 \rho_s}\right\} \tag{11}$$

The assumption of a value for the density of tungsten, ρ_s, at 26.68°C, $\rho_s = 19148.6\ \mathrm{kg \cdot m^{-3}}$, the adoption of literature values for E [4], and the measurement of $2L$ with a cathetometer then permit the measurement of ω_0 at the same temperature to be used to determine R. The value determined in this way, $R = 49.953\ \mu$m, is within the error of a direct determination with a projection microscope, $R = 50.0 \pm 1\ \mu$m.

It should be noted that it is the group, $\rho_s R^2$, which is most sensitively determined by this procedure because the second term in Eq. (11) is very much smaller than the first. Furthermore, within the fundamental working Eqs. (1) and (2), it is again the group $R^2 \rho_s$ which occurs in the dominant contribution to the change in the resonant frequency when the assembly is immersed in a fluid. Consequently, the particular values of R and ρ_s assigned in this procedure are of relatively small significance compared with the value of their combination $R^2 \rho_s$, determined directly by the calibration described above.

The volume of the weight, V_w, has been determined by measurement of the resonant frequency of the wire when the assembly is immersed in *n*-octane at 25.68°C and a pressure of 0.1 MPa. Dymond et al. [5] have reported accurate density data so that a reference value $\rho = \rho_{\mathrm{ref}}$ can be adopted and the working Eqs. (1) and (2) solved to yield V_w. The value derived in this way is listed in Table I, which contains all the other characteristics of the oscillating system.

3.3. Application of Corrections

In order to apply the densimeter over a range of temperatures and pressures, it is necessary to introduce a number of very small corrections

Table I. Solid Material Properties of the Vibrating-Wire Densimeter and Its Resonant Characteristics *in Vacuo*

	$T = 298.83$ K	$T = 323.15$ K
Tungsten wire		
Radius (μm)[a]	49.953	49.958
Length (mm)	43.75	43.76
Density ($\mathrm{kg \cdot m^{-3}}$)	19148.6	19142.1
Young's modulus (GPa)	406.1	405.3
Aluminium weight		
Mass (kg)	0.14818	0.14818
Volume ($\mathrm{cm^3}$)[a]	49.853	49.939
Resonant characteristics *in vacuo*		
Resonant frequency (Hz)	1132.62	1132.51
Dimensionless internal damping coefficient (−)	7.1×10^{-5}	6.0×10^{-5}

[a] Deduced by calibration at $T = 298.83$ K.

to the characteristics of the instrument. Thus, it is necessary to correct the volume of the aluminium weight, the density of aluminium and of tungsten, and the radius of the wire and its length for temperature and pressure changes. The temperature changes have been accommodated using coefficients of linear expansion for the metals [4], while the effects of pressure are accommodated with the aid of values for the isothermal compressibility [4]. Table I includes the values of the characteristics of the instrument deduced by applying those corrections for a temperature of 323.15 K, illustrating the small magnitude of the corrections for temperature. The effects of pressure are of a similar magnitude for a pressure change of 100 MPa so that in both cases their evaluation contributes negligibly to the uncertainty in the measured density.

The final correction to be applied arises from a different source, namely, the fact that the wire oscillates in a fluid bounded by a surface at a finite distance. In practice, this boundary surface is a complicated shape (Fig. 2), owing to the presence of the magnets, so that it is not possible to use the theory available for a finite cylindrical enclosure of radius R_c [2]

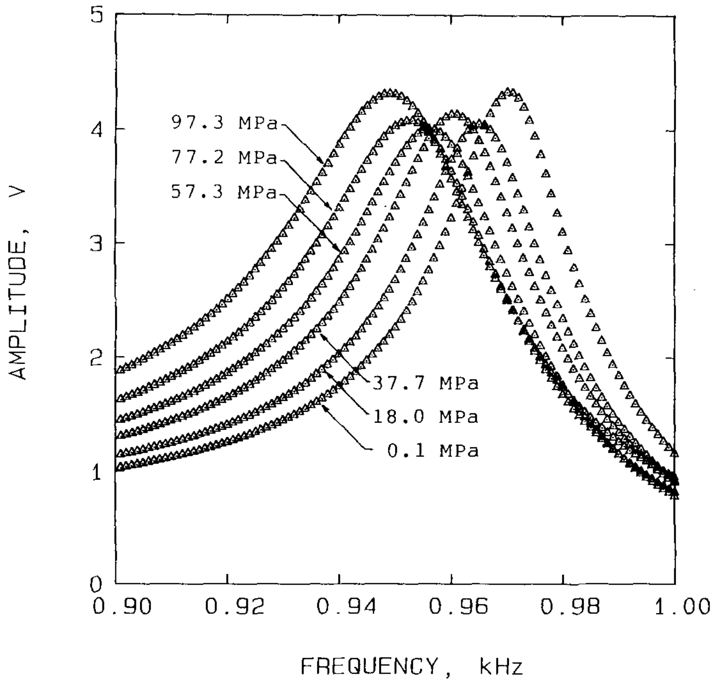

Fig. 5. A sequence of resonance curves for the wire in *n*-octane over a range of pressures.

directly. Instead, the design of the magnet enclosure has been such that the magnet faces are the nearest surfaces to the vibrating wire at a distance, *d*. The distance *d* has then been chosen so that, if a complete cylindrical enclosure was placed at a radius $R_c = d$ around the wire, the correction to the density arising from the presence of the finite boundary would not amount to more than ±0.1%. In these circumstances, the theory for a finite cylindrical enclosure [2] can be employed to estimate the correction to the result for an infinite enclosure in a way that introduces insignificant error into the final fluid density.

3.4. The Measurements

In order to demonstrate the precision and reproducibility of the present instrument, two series of measurements of the density of normal octane have been carried out along two isotherms, 298.83 and 323.15 K, at pressures up to about 100 MPa. The *n*-octane samples were provided by BDH Chemicals Ltd. with a purity in excess of 99.9% and were further purified and degassed before use. The viscosity of *n*-octane required for the

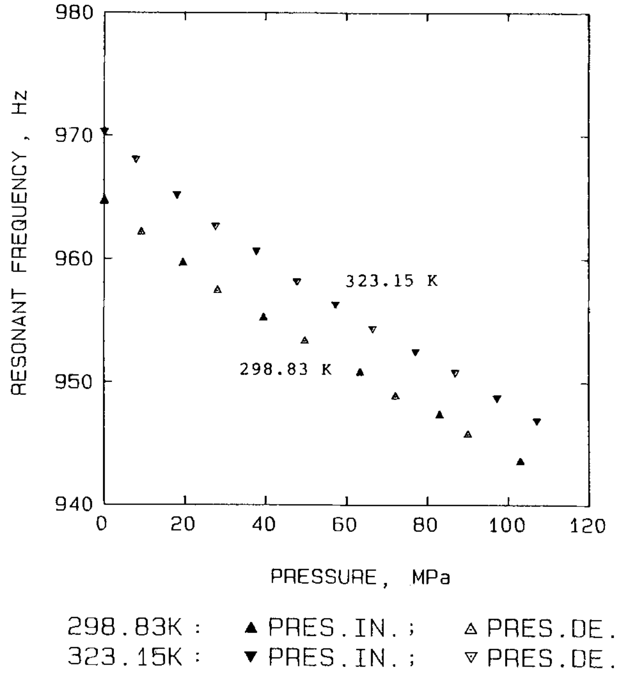

Fig. 6. The effects of pressure cycling on the resonant frequency of the wire.

analysis of the results has been taken from the work of Kashiwagi and Makita [6].

As indicated earlier, a measurement of the resonant frequency and the resonance width was made *in vacuo* at each temperature prior to measurements with the liquid. Figure 5 shows a sequence of resonance curves for measurements in *n*-octane at the lower temperature, indicating the decrease in resonant frequency and increase in width increasing pressure. In this series of measurements the driving voltage was adjusted at each pressure to secure approximately the same peak signal so as to preserve a high signal-to-noise ratio. In other sequences the driving voltage was maintained ambient for all pressures so that the peak response diminished with increasing pressure. These tests demonstrated a marginal gain in precision for the former procedure, which was therefore usually adopted.

Table II. The Density of *n*-Octane at $T = 298.83$ K and $T = 323.15$ K

Temperature T (K)	Pressure P (MPa)	Resonant frequency ω_r (Hz)	ρ (kg·m^{-3}) Present work	ρ (kg·m^{-3}) Ref. 5
298.83	0.1[a]	964.7	697.9	698.1
	0.1	964.6	697.7	698.1
	9.2	962.1	706.3	705.8
	19.5	959.6	714.2	713.9
	28.1	957.4	721.3	720.0
	39.6	955.2	727.8	727.6
	49.8	953.3	733.2	733.9
	63.4	950.7	740.6	741.5
	72.2	948.8	746.5	746.0
	83.1	947.3	750.6	751.4
	90.1	945.7	755.1	754.6
	103.0	943.5	761.2	760.3
323.15	0.1	970.3	678.4	678.3
	0.1	970.3	678.5	678.3
	7.9	968.1	686.1	686.1
	18.0	965.2	696.0	695.2
	27.6	962.7	704.5	703.1
	37.7	960.7	710.7	710.7
	47.8	958.2	718.9	717.6
	57.3	956.3	724.7	723.5
	66.5	954.4	731.1	728.9
	77.2	952.5	736.6	734.8
	87.0	950.8	741.8	739.8

[a] Value employed for calibration.

One of the principal benefits to be expected of the present densimeter is a gain in reproducibility upon cycling of the pressure compared with densimeters in which the fluid is internal to an enclosure. This benefit arises from the fact that the effects of the pressure are confined to hydrostatic forces of compression on solid bodies which are less prone to hysteresis. Figure 6 shows the effects of pressure cycles on the resonant frequency of the wire for both isotherms studied for *n*-octane. Over all of the cycles conducted, the resonant frequency for a particular pressure was reproducible to within ±0.2 Hz, which is commensurate with the precision of an individual measurement. It is therefore concluded that there are no significant effects of hysteresis in the present instrument.

4. RESULTS

Table II contains the results of the present measurements of the density of *n*-octane along isotherms at 298.83 and 323.15 K. In the same table we list the results interpolated from the tables of Dymond et al. [5] for the density of *n*-octane, which have an estimated uncertainty of ±0.1–0.2%, indicating the single value at atmospheric pressure used for calibration. Figure 7 compares the results of the present measurements with those of Dymond et al. [5], and it can be seen that along the lower isotherm the agreement is within ±0.2%—that is, within the mutual uncertainty of the

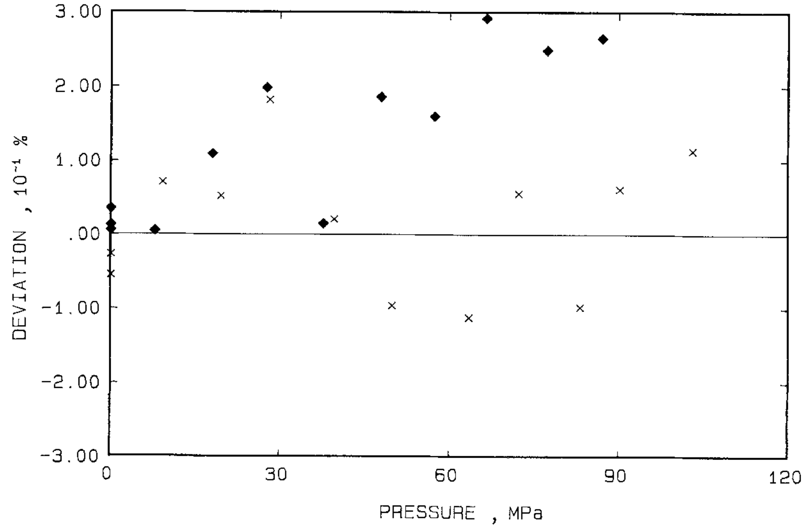

Fig. 7. Deviations of the present data for the density of *n*-octane from the measurements of Dymond et al. [5]. (×) 298.83 K; (◆) 323.15 K.

two sets of data. Along the higher isotherm the agreement is of a similar order up to 85 MPa. This represents a satisfactory demonstration that the instrument operates in accordance with the theoretical model of it and is capable of measurements with an accuracy of ±0.2% when used in the relative manner described.

5. CONCLUSIONS

A new type of vibrating-wire densimeter has been designed and constructed for measurements on liquids at high pressures. The first set of results presented here indicates that if the instrument is operated in a relative mode, measurements of the density with an accuracy of ±0.2% can be achieved at pressures up to 100 MPa. Operation in this relative manner requires the determination of two instrument parameters by calibration using just one datum for the density of a single liquid. Since the operating principle is so simple, there seems every reason to expect that operation over a wider range of conditions should be possible with the present instrument. Of course, the principle of the method has a potentially even greater range of application, for example, at high temperatures and in gaseous materials.

ACKNOWLEDGMENTS

The authors acknowledge partial financial support for this work from the U.K. Department of Trade and Industry and JNICT in Portugal. In addition, they wish to thank Mr. A. Pushman for his valuble contributions to the construction of the instrument and Mr. I. Drummond for his assistance with the analysis of the liquid samples.

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