

## **Validation of an Accurate Vibrating-Wire Densimeter: Density and Viscosity of Liquids Over Wide Ranges of Temperature and Pressure**

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A new vibrating-wire instrument for the measurement of the density of fluids at high pressures was described in a previous paper. The technique makes use of the buoyancy force on a solid sinker and detects this force with a vibrating wire placed inside the measuring cell. Owing to the simple geometry of the oscillating element there exists a complete theoretical description of its resonance characteristics, enabling the calculation of the density of the fluid from their measurement. In the present paper a new method for the determination of the cell constants is outlined which permits the operation of the densimeter essentially as an absolute instrument. Furthermore, it is shown that the viscosity of the fluid can be measured simultaneously with the density. New results for three fluids are presented: for cyclohexane at temperatures from 298 to 348 K and pressures up to 40 MPa, for 2,2,4-trimethylpentane between 197 and 348 K at 0.1 MPa, and for 1,1,1,2-tetrafluoroethane from 197 to 298 K close to saturation. The sets of measurements were chosen with the intention of testing the performance of the apparatus, complementing previous work at higher pressures. The densities and viscosities measured exhibit the same accuracy for all of the three fluids over the entire temperature and pressure ranges and were obtained using the same set of cell parameters. The precision of the densities is  $\pm 0.03\%$  and their estimated accuracy is  $\pm 0.05\%$ . The viscosities have a precision of  $\pm 0.6\%$  and an estimated accuracy of  $\pm 2\%$ .

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**KEY WORDS:** cyclohexane; density; liquid;  $p/T$ ; 1,1,1,2-tetrafluoroethane (R134a); 2,2,4-trimethylpentane; vibrating-wire densimeter; viscosity.

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## 1. INTRODUCTION

In an earlier paper [1], the initial development of a vibrating-wire densimeter was reported, together with the results of a set of measurements in 2,2,4-trimethylpentane along three isotherms from 298 to 348 K and up to 100 MPa. That earlier paper concentrated upon instrumental refinements designed to improve the precision of the technique and preserve it over wide ranges of conditions. That paper contains details of the technique and the experimental procedure.

The present paper is devoted in part to a demonstration that the apparatus operates in detail in accord with a theoretical model of it which is derived from a complete description of the underlying working principles. Such a demonstration is an essential prerequisite to the performance of absolute measurements of the density of a fluid and of its viscosity. A second feature of absolute measurements is that the characteristics of the instrument, as distinct from those of the fluid, which enter the evaluation should themselves be well characterized, determined by one or more independent measurements, and remain unchanged when the instrument is operated under different conditions of temperature and pressure and with different fluids. In order to confirm that the new instrument conforms to these characteristics, measurements have been performed in three different fluids, at temperatures from 197 to 348 K and pressures up to 40 MPa. The liquids have been selected in such a way that their densities and viscosities cover a wide range of values and for which some reliable data already exist.

According to the most recent theory of the vibrating-wire densimeter [2, 3], the observed electrical signals can be related directly to mechanical effects and thereby to the density and viscosity of the fluid that surrounds the wire. In this particular paper, we devote great attention to the extent by which the instrument conforms to its theoretical model. Having confirmed this fact the intrinsically absolute value of the densimeter and its wide range of applicability are emphasized.

## 2. WORKING EQUATIONS

### 2.1. Resonance Condition

The theoretical treatment of the motion of a vibrating wire was first considered for the development of a fluid densimeter by Retsina, et al. [4]. In their analysis the model of the densimeter, intended to be an accurate representation of a true instrument, envisaged a solid cylindrical rod subject to an axial tension and to a harmonic driving force in a direction perpendicular to the axis. The wire is then forced to undergo transverse,

steady oscillations immersed in a Newtonian fluid with a fixed density and viscosity. The analysis of the total motion was simplified by separating the motion of the wire from that of the fluid [4]. The wire motion was treated applying solid continuum mechanics of a thin beam [2, 4, 5]. The motion of the fluid was treated with the slow flow limit through a solution of the linearized Navier–Stokes equation. The result of this analysis is a complete description of the motion of the wire and fluid in a well-defined set of circumstances. It was originally expressed in the displacement of the wire at each point along its length as a function of time in each one of a set of vibration modes [4].

In practice, a metallic wire is used as the vibrating element and it is forced to move by means of a current of an appropriate frequency applied along the wire in the presence of a permanent magnetic field. The electromotive force induced across the ends of the wire, owing to its motion, is a measure of the wire velocity in the fundamental mode. This velocity may be obtained simply from the results of Retsina et al. [4], by differentiation of the dimensionless displacement,  $\zeta_0$ , with respect to dimensionless time,  $\tau$ ,

$$\dot{\zeta}_0 = \frac{i\tilde{\omega}F_0^*(\zeta) e^{i\tilde{\omega}\tau}}{\tilde{\omega}_0^2 - \tilde{\omega}^2(1 + \beta) + i\tilde{\omega}^2(\beta' + 2\mathcal{A}_0)} \quad (1)$$

where  $\tilde{\omega}$  is a dimensionless frequency,  $\tilde{\omega}_0$  is the natural frequency (under total absence of damping),  $F_0^*$  describes the driving force, and  $\zeta$  is the dimensionless coordinate along the wire.  $F_0^*$  is an arbitrary function of position along the wire. The group  $(1 + \beta)$  is the dimensionless inertial term, where  $\beta = k\rho/\rho_s$  accounts for the added mass owing to the presence of the fluid ( $\rho$  and  $\rho_s$  are the density of the fluid and of the wire material, respectively, and  $k$  is a function of the Reynolds number associated with the flow) [4]. The damping is given by the group  $(\beta' + 2\mathcal{A}_0)$ , where  $\beta' = k'\rho/\rho_s$  is the contribution of the fluid ( $k'$  is another function of the Reynolds number) and  $\mathcal{A}_0$  is the internal damping owing to inelasticity of the wire material.

The dimensionless frequencies for small oscillations are obtained from the angular frequencies using the relation

$$\tilde{\omega} = \omega \sqrt{\frac{2\rho_s L^4}{ER^2}} \quad (2)$$

where  $E$  is Young's modulus of the wire material,  $R$  its radius, and  $L$  its half-length.

Under steady-state forced oscillations, the relevant function to describe the frequency behavior of the velocity amplitude results from a simple rearrangement of Eq (1):

$$\dot{\xi}_0 = \frac{F_0^*(\zeta) e^{i(\tilde{\omega}\tau - \varphi)}}{\{(1/\tilde{\omega}^2)[\tilde{\omega}^2(1 + \beta) - \tilde{\omega}_0^2]^2 + \tilde{\omega}^2(\beta' + 2\Delta_0)^2\}^{1/2}} \quad (3)$$

where the phase of the velocity relative to the driving force is

$$\varphi = \tan^{-1} \left( \frac{\tilde{\omega}^2(1 + \beta) - \tilde{\omega}_0^2}{\tilde{\omega}^2(\beta' + 2\Delta_0)} \right) \quad (4)$$

Velocity resonance occurs at the frequency  $\tilde{\omega}_r$ , that satisfies [1, 6]

$$\frac{d}{d\tilde{\omega}} \left\{ \frac{1}{\tilde{\omega}^2} [\tilde{\omega}^2(1 + \beta) - \tilde{\omega}_0^2]^2 + \tilde{\omega}^2(\beta' + 2\Delta_0)^2 \right\} = 0 \quad (5)$$

If we define  $\tilde{R} = \tilde{\omega}(\beta' + 2\Delta_0)$ ,  $\tilde{M} = 1 + \beta$ , and  $\tilde{K} = \tilde{\omega}_0^2 \tilde{M}_{\beta=0}$ , then we can write

$$\dot{\xi}_0 = \frac{F_0^*(\zeta) e^{i\tilde{\omega}\tau}}{\tilde{R} + i\tilde{\omega}\tilde{M} + (\tilde{K}/i\tilde{\omega})} \quad (6)$$

which is evidently the velocity behavior of the general forced harmonic oscillator [7]. In the present case the oscillator has essentially distributed, and not lumped, properties and the contributions owing to the fluid are a function of the wire velocity, so it is natural to have frequency-dependent effective mass,  $\tilde{M}$ , and resistance,  $\tilde{R}$ .

If we define  $\tilde{\gamma} = \tilde{R}/\tilde{M}$ , then the absolute value of the complex velocity can be written as

$$|\dot{\xi}_0| = \frac{F_0^*}{\tilde{R}} \left[ \frac{\tilde{\omega}^2 \tilde{\gamma}^2}{\tilde{\omega}^2 \tilde{\gamma}^2 + (\tilde{\omega}^2 - \tilde{\omega}_0^2)^2} \right]^{1/2} = \frac{F_0^*}{\tilde{R}} [f(\tilde{\omega})]^{1/2} \quad (7)$$

where  $f(\tilde{\omega})$  is a response function [7] whose values lie in the interval  $0 \leq f(\tilde{\omega}) \leq 1$ , with  $f(0) = f(\infty) = 0$  and  $f(\tilde{\omega}_0) = 1$ . The two frequencies at which  $f(\tilde{\omega}_{\pm}) = \frac{1}{2}$  are such that  $\tilde{\omega}_+ - \tilde{\omega}_- = \tilde{\gamma}$  and therefore  $\tilde{\gamma}$  is the width at half-height of the response function [7]. It is useful to evaluate the amplitude of the power dissipated in each cycle, which is given by [2, 7]

$$\tilde{P} = \tilde{R} |\dot{\xi}_0|^2 = \frac{F_0^{*2}}{\tilde{R}} f(\tilde{\omega}) \quad (8)$$

which shows that  $\tilde{\gamma}$  is also the width at half of the height of the power curve.

Equation (7) represents the velocity resonance curve to be expected for a wire vibrating in a viscous fluid. Thus, if it is possible to determine the resonance curve  $|\xi_0(\tilde{\omega})|$ , then it is possible to determine the three free parameters  $\tilde{\omega}_0$ ,  $\tilde{\gamma}$  and  $F_0^*/\tilde{R}$  from a fit of Eq. (7) to the data. The first two can be used to derive two working equations: one is the resonance condition, Eq. (5), and the other relates the frequencies,  $\tilde{\omega}_\pm$ , at which the power amplitude is one-half of its maximum value, to the resonant frequency,  $\tilde{\omega}_r$ . Since, from Eq. (8),

$$\tilde{P}(\tilde{\omega}) \propto \frac{\tilde{\omega}(\beta' + 2\Delta_0)}{(1/\tilde{\omega}^2)[\tilde{\omega}^2(1 + \beta) - \tilde{\omega}_0^2]^2 + \tilde{\omega}^2(\beta' + 2\Delta_0)^2} \quad (9)$$

then the equations for the frequencies at half-power become

$$\begin{aligned} & \frac{\tilde{\omega}_\pm(\beta' + 2\Delta_0)}{(1/\tilde{\omega}_\pm^2)[\tilde{\omega}_\pm^2(1 + \beta) - \tilde{\omega}_0^2]^2 + \tilde{\omega}_\pm^2(\beta' + 2\Delta_0)^2} \\ &= \frac{1}{2} \frac{\tilde{\omega}_r(\beta' + 2\Delta_0)}{(1/\tilde{\omega}_r^2)[\tilde{\omega}_r^2(1 + \beta) - \tilde{\omega}_0^2]^2 + \tilde{\omega}_r^2(\beta' + 2\Delta_0)^2} \end{aligned} \quad (10)$$

where  $\tilde{\omega}_r$  is the resonant frequency in the presence of damping, and  $\tilde{\omega}_\pm$  is either  $\tilde{\omega}_+$  or  $\tilde{\omega}_-$ . Equations (5) and (10) are the basic working equations for the vibrating-wire instrument in steady-state mode.

Because the present work is concerned with the measurement of the velocity of the resonator, it is necessary to develop a new method of determining the internal damping coefficient of wire oscillations from the resonance curve under vacuum. Under these conditions the resonant frequency,  $\omega_1$ , will be slightly shifted from the natural frequency,  $\omega_0$ , owing to internal damping. The two equalities in Eq. (10), applied for the oscillations under vacuum, can be combined to yield an expression for the width of the power curve,  $\gamma_1$ . The internal damping coefficient will be given by

$$\Delta_0 = \frac{1}{2} \left\{ \frac{1}{2 - [1 + (\gamma_1/\omega_1)^2]^{1/2}} - 1 \right\}^{1/2} \quad (11)$$

The natural frequency itself can also be calculated from the resonant frequency under vacuum by means of application of Eq. (5), to yield

$$\tilde{\omega}_0 = \tilde{\omega}_1(1 + 4\Delta_0^2)^{1/4} \quad (12)$$

Thus, the two parameters  $\Delta_0$  and  $\omega_0$  can be obtained experimentally from the resonance characteristics under vacuum.

## 2.2. Hydrodynamic Effects

In Section 2.1 the effects of fluid flow around the vibrating wire were assumed to be known and expressed in terms of two quantities,  $k$  and  $k'$  [4]. The first of these contains the inertial contribution and the second the viscous drag. They are given by

$$\begin{aligned} k &= -1 + 2 \operatorname{Im}(A) \\ k' &= 2 \operatorname{Re}(A) \end{aligned} \quad (13)$$

The complex quantity  $A$  depends on the modified Bessel functions  $K_0$  and  $K_1$  of a dimensionless group  $\Omega$ :

$$A = i \left\{ 1 + \frac{2K_1(\sqrt{i\Omega})}{\sqrt{i\Omega} K_0(\sqrt{i\Omega})} \right\} \quad (14)$$

$\Omega$  is closely related to the Reynolds number and is given by

$$\Omega = \frac{\rho\omega R^2}{\eta} \quad (15)$$

where  $\eta$  is the viscosity of the fluid.

## 2.3. Effects of Buoyancy

It can be seen from the analysis above that from measurements of the displacement or velocity resonance curves of a vibrating wire, the density of a fluid and/or its viscosity can be determined if the radius, length, and density of the wire are known. This has been applied in practice [8] but lacks sensitivity to the density of the fluid.

The sensitivity of a vibrating-wire densimeter can be enhanced if, in addition to direct hydrodynamic action in the wire, one makes use of hydrostatic buoyancy forces acting on a sinker suspended from its lower end under gravity. This is because changes in the buoyancy force caused by fluid density alterations are transmitted to the wire as changes in the tension to which it is subjected and thereby directly to its resonant frequency. The introduction of this buoyancy mechanism clearly has no effect on the results of the treatment of the fluid mechanics for the wire. Thus,  $k$  and  $k'$  calculated according to Retsina et al. [4] remain valid.

The buoyancy effect can be incorporated into the treatment in Section 2.1 if  $\omega_0$  is replaced by another resonant frequency,  $\omega_B$ , which corresponds

to the hypothetical situation of having the wire oscillating under total absence of damping, but under reduced tension owing to the buoyancy effect [1, 6],

$$\omega_B^2 = \omega_0^2 - \frac{\pi g \rho}{4L^2 \rho_s R^2 \rho_w} \quad (16)$$

where  $\rho$  is the density of the fluid and  $\rho_w$  is the density of the sinker.

The gain in sensitivity from the use of the buoyancy effect is seen from the fact that in the present instrument, of the shift in resonant frequency from that under vacuum to that in a typical organic liquid, more than 80% arises from buoyancy and less than 20% from hydrodynamic effects.

The characteristic of the steady-state resonance curve which is most closely related to the viscous damping is the width of the peak. It is noteworthy that vibrating-wire viscometers based on the same theoretical model but using instead the transient-decay mode have been built [9, 10]. Generally, a device to compensate for the buoyancy effect has been adopted in an attempt to maintain the resonant frequency as constant as possible, therefore achieving an arrangement where it is the sensitivity to the hydrodynamic effect that becomes the most important. This cannot be a necessary condition for the operation of a successful viscometer.

The ability of the present instrument, which has been designed primarily as a densimeter, simultaneously to measure the viscosity is a particularly important feature. Otherwise, the utilization of the technique would be restricted to fluids of known viscosity (although, by means of an adequate instrument design, without need of a high accuracy). An equivalent, complementary problem has been faced by investigators using oscillating-disk viscometers and successfully solved [11]. No fundamental difference exists between the vibrating-wire densimeter and viscometer. Instead, the design approaches have led to a different balance of the sensitivities, to either the density or the viscosity. It is an additional purpose of the present work to investigate whether the sensitivity of the present instrument to viscosity is enough for a precise simultaneous determination of this property. It is not expected that a densimeter can attain the same precision in viscosity that can be reached with a purpose-built vibrating-wire viscometer.

The foregoing analysis of the theory of the densimeter making use of buoyancy in conjunction with a vibrating wire establishes the basis for absolute measurements of the density of fluids if it can be shown that a practical instrument conforms to the theory. For this reason we report here measurements of the density and viscosity of three liquids over a range of conditions.

### 3. EXPERIMENTS

The vibrating-wire densimeter employed for the measurements has been described in detail elsewhere [1]. A glass pycnometer with a volume of about 60 cm<sup>3</sup> was used to produce independent measurements of the sample densities at 298.15 K and 0.1 MPa, serving also as a purity test. The pycnometer follows the design of Ostwald or Lipkin: it consists of a bulb with two capillary outlets, one connected to its top and the other to its bottom. Using this arrangement the pycnometer can be filled and emptied without retaining air bubbles. The lower capillary is bound around the bulb and both capillaries terminate in graduated parallel segments. The pycnometer is filled up to a certain graduation, and its horizontal position defined by the two parallel scales. Its volume was calibrated with distilled water and distilled mercury [2].

The sample of 2,2,4-trimethylpentane was prepared from 2.5 l of isooctane p.a. from Merck (stated purity, 99.5%). It was dried over 4-Å molecular sieves, distilled under a nitrogen atmosphere over calcium hydride, and finally, degassed using a helium disperser. The stated purity was confirmed by chromatography and the final purity was 99.7%. The density at 298.15 K and 0.1 MPa was assessed with the pycnometer and a value of  $687.84 \pm 0.05 \text{ kg} \cdot \text{m}^{-3}$  was obtained. The value recommended by IUPAC [12] for a sample of 2,2,4-trimethylpentane with a similar purity (99.75%) is  $687.85 \text{ kg} \cdot \text{m}^{-3}$ .

The sample of cyclohexane was prepared from 2.5 l of Aldrich HPLC reagent, of stated purity 99.85%. Owing to the high purity of the initial product, it was used without further purification except for the degassing. Its density was measured with the pycnometer, at 298.15 K and 0.1 MPa, and the result was  $773.74 \pm 0.05 \text{ kg} \cdot \text{m}^{-3}$ . The value recommended by IUPAC [12] for cyclohexane (purity of 99.98%) is  $773.89 \text{ kg} \cdot \text{m}^{-3}$ .

The 1,1,1,2-tetrafluoroethane (HFC134a) used for the measurements was taken from a round-robin sample [13] of stated purity 99.9% and was used without further purification. In all cases, the cell of the vibrating-wire densimeter was filled under vacuum through a 65- $\mu\text{m}$  filter to avoid contamination or the admission of solid particles to the interior of the pressure vessel containing the densimeter. A volume of about 100 cm<sup>3</sup> is necessary to fill the vessel.

Above room temperature, a thermostatic oil bath was used for temperature control [1, 2]. For the lower temperatures, a new thermostatic system was built, based on a circulation cryostat [2]. The temperature of the circulating fluid was controlled to within  $\pm 0.05 \text{ K}$ , and owing to the large thermal inertia of the metal vessels employed, the fluctuations in the temperature on the outside of the pressure vessel were typically within



$\pm 0.002$  K during the acquisition of one datum and within  $\pm 0.01$  K on a time scale of several days (roughly the same stability was attained with the oil bath).

Temperature was measured using a 100- $\Omega$  platinum resistance thermometer, calibrated at the triple point of water and by comparison with a Tinsley 5187L 25- $\Omega$  thermometer, which had been calibrated at the National Physics Laboratory, UK. The accuracy of the temperature readings is better than 0.01 K. Pressures up to 32 MPa were measured using a capacitance transducer with a resolution of 0.01 MPa and an accuracy of 0.02 MPa. Above this point, a Heise Bourdon tube manometer was used, and in this range the accuracy is of 0.07 MPa. Both manometers were calibrated against a Ruska 2450 deadweight gauge.

#### 4. DETERMINATION OF THE CELL PARAMETERS

The working Eqs. (5), (10), and (13) contain eight quantities characteristic of the densimeter and independent of any fluid. They are  $\omega_0$ ,  $\Delta_0$ ,  $E$ ,  $L$ ,  $R$ ,  $\rho_s$ ,  $\rho_w$ , and  $M_w$  (the latter two parameters are the density and mass of the sinker, respectively). Once these are known, the density and viscosity of a fluid can be obtained at any pressure and temperature from measurement of the resonant frequency of the wire and the width of the resonance curve. A sensitivity analysis was conducted to evaluate the accuracy required in each of these parameters to keep errors in the measured density below  $\pm 0.1\%$ . Table I contains such values for these parameters where there is a significant contribution to the uncertainty in the density. The mass of the sinker was omitted because it can be determined by direct weighing with an accuracy of less than 1 ppm, so its error will be negligible. The frequency of oscillation can be determined in our installation with an uncertainty of  $\pm 0.005\%$ , so its contribution to the error in the density becomes clear from Table I. The length of the wire (approx 4 cm) can be determined with an accuracy of  $\pm 0.05\%$  using a cathetometer which is adequate for the present purposes. The internal damping coefficient and the Young's modulus of the wire material (tungsten) cannot be known very accurately, but uncertainties of one order of magnitude have no significant effect upon the evaluation of the fluid density.

Table I. Admissible Variations in Cell Parameters to Keep Errors in Density Below  $\pm 0.1\%$

$\eta$	$L$	$R$	$\rho_s$	$\rho_w$	$\omega$
$\pm 3\%$	$\pm 0.05\%$	$\pm 0.05\%$	$\pm 0.1\%$	$\pm 0.09\%$	$\pm 0.025\%$

For the remaining three parameters,  $R$ ,  $\rho_s$  and  $\rho_w$  it would be difficult to achieve the necessary accuracy by independent methods. First, the wire has a nominal radius of only  $50\ \mu\text{m}$  so that it is practically impossible to attain the precision required in its measurement. Furthermore the uniformity of the radius along the length of the wire is unknown. It is also difficult to determine its density owing to the minute volume of the sample of wire.

As has been pointed out [1, 6], values for the radius and density of the wire need not be very accurate individually because these two parameters appear as a group ( $R^2\rho_s$ ) in the most significant contribution (that of the buoyancy effect)—see Eq. (16). Therefore, a literature value for the density of the wire (in the present case, composed of 99.95% pure tungsten) can be adopted.

The sinker consists of a carefully machined aluminium cylinder with a volume of about  $55\ \text{cm}^3$ , but the only successful clamping mechanism devised required the use of a miniature stainless-steel chuck mounted on the sinker. Owing to this fact, the volume of the arrangement cannot be easily determined with the accuracy stated in Table I.

These arguments mean that there are two characteristic parameters of the instrument,  $R$  and  $\rho_w$ , whose independent measurement would render the absolute determination of fluid densities possible. It is our view that such independent measurements could be carried out by virtue of great effort and expense. However, practicality dictates that rather more convenient means be found to determine the two parameters. The two fundamental working equation, Eqs. (5) and (10), of the theoretical model of the instrument make this possible because, from the determination of the resonance curve in one fluid at one temperature and pressure, where the density and viscosity of the fluid are known, both  $R$  and  $\rho_w$  can be evaluated. This one experiment in a reference fluid, which can be performed at room temperature and atmospheric pressure, should not be understood as a calibration in the same sense as applied to purely relative densimeters. This is the case because the vibrating-wire densimeter is described by a complete, rigorous model.

The radius of the wire and the volume of the weight show different sensitivities to the properties of the fluid: the volume of the weight is directly related to the buoyancy effect and affects predominantly the value of the resonant frequency. The radius of the wire is related also to the hydrodynamic effect, which is largely a result of damping owing to viscous forces. Thus, although the two equations are solved simultaneously for the two parameters, the volume of the weight will be determined mainly by the density of the reference fluid, and the radius of the wire mainly by its viscosity.

For this work the reference experiment was performed in 2,2,4-trimethylpentane at 298.15 K and 0.1 MPa, with a sample of the fluid

Table II. Parameters of the Densimeter Cell at 298 K

Wire: tungsten	
Length (m)	$41.48 \times 10^{-3}$
Radius (m)	$48.58 \times 10^{-6}$
Density ( $\text{kg} \cdot \text{m}^{-3}$ )	19230
Young's modulus (Pa)	$0.41 \times 10^{12}$
Sinkers: aluminium	
Mass (kg)	0.154951
Density ( $\text{kg} \cdot \text{m}^{-3}$ )	2735.7
Resonance under vacuum	
Frequency (Hz)	1279.93
Half-width (Hz)	0.39
Internal damping coefficient	$0.5 \times 10^{-4}$

prepared as indicated above. The density of the reference fluid had been measured independently using the pycnometer and the reference value indicated previously was obtained. The viscosity of this sample under the same conditions was measured using a capillary viscometer, resulting in a reference viscosity of  $0.472 \pm 0.003$  mPa · s. The resonant frequency was 1087.13 Hz and the width at half-height was 24.83 Hz. The complete set of cell constants is listed in Table II, including those determined from the single reference experiment.

The calculated value for the density of the sinker coincides with the value determined roughly by weighing in an analytical balance, first in air and then immersed in a liquid of known density, which resulted in an estimate of  $2732 \text{ kg} \cdot \text{m}^{-3}$ . The value for the radius of the wire is smaller than the nominal value by about 3%. Table I shows that this is commensurate with the sensitivity of the instrument to the viscosity of the fluid, which is the property that largely determines the wire radius. These two facts on their own suggest that the working equations describe the instrument satisfactorily.

## 5. RESULTS

### 5.1. Validation of Operation

It is a further prerequisite of the use of the instrument for accurate density measurements on fluids that the resonance curve determined from oscillations in a fluid should be entirely consistent with the description provided by Eq. (1). As indicated elsewhere [1, 2] the resonance curves are deduced by standard electrical techniques, and one such, obtained in a typical liquid, is shown in Fig. 1. The direct electrical impedance

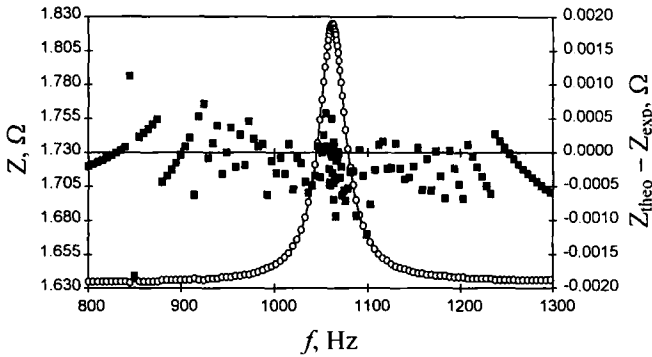


Fig. 1. Typical resonance curve in terms of the electrical impedance of the vibrating wire. (○) Experimental points; (—) theoretical model (left  $y$ -axis); (■) deviations (right  $y$ -axis).

measurements,  $Z$ , are shown as points, and the solid line results from the fitting of the theoretical model. The absolute value of the electrical impedance, which is a manifestation of the wire oscillating inside a permanent magnetic field, is given by

$$Z(\omega) = \left[ \frac{(R + R_1)^2 \gamma^2 \omega^2 + R_1^2 (\omega^2 - \omega_0^2)^2}{\gamma^2 \omega^2 + (\omega^2 - \omega_0^2)^2} \right]^{1/2} \quad (17)$$

where  $R_1$  is the ohmic resistance of the wire and the resistance  $R$ , the resonant frequency  $\omega_0$ , and the width  $\gamma$  define a resonator. Equation (17) is deduced in terms of the theoretical model elsewhere [2]. The relations between the mechanical behavior of the wire and the observed electrical properties will be the subject of a future publication.

Because the two curves in Fig. 1 are indistinguishable on the scale of the graph the deviations are also shown. The deviations are of a similar order as the resolution of the instrument used for the electrical measurements, as can be seen from the behaviour of the deviations near the limits of the frequency interval. This result, which is repeated for every measurement performed, is taken as evidence that the instrument operates in accord with the theoretical model.

## 5.2. Density Measurements

The validation of the instrument is completed by means of a comparison of the present measurements with those obtained by independent authors for a number of different liquids over a range of conditions. For that reason we confine the presentation of experimental results here to conditions where such a comparison is possible.

In the cases of 2,2,4-trimethylpentane and 1,1,1,2-tetrafluoroethane, this restricts the comparisons to atmospheric pressure and/or the saturation line. For cyclohexane comparisons are made up to 40 MPa. Temperatures range from 200 to 350 K.

### 5.3. Cyclohexane

The data for cyclohexane consist of five isotherms up to the freezing pressure at room temperature. The densities and viscosities are listed in Table III, together with the resonant frequencies  $f_r$  and widths  $\gamma$ . The densities along each isotherm were correlated using the Tait equation [14]:

$$\frac{\rho - \rho_0}{\rho} = C \log \frac{B + p}{B + p_0} \quad (18)$$

The viscosities were correlated using an equation similar to the Tait equation,

$$\ln \frac{\eta}{\eta_0} = E \ln \frac{D + p}{D + p_0} \quad (19)$$

The optimized coefficients for these equations are presented in Tables IV and V. The maximum deviation observed for the densities is  $\pm 0.05\%$  and the standard deviation,  $\sigma$ , is of  $\pm 0.03\%$ , while the deviations of the viscosities are smaller than  $\pm 0.3\%$ .

The densities at 0.1 MPa were correlated with a polynomial equation of the form

$$\rho_0(T) = \sum_{i=0}^n d_i T^i \quad (20)$$

whose coefficients are listed in Table VI.

In the Tait equation the behavior of each isotherm along the pressure range is modeled by the parameter  $B$ , which generally exhibits a smooth behavior with temperature. At the critical isotherm,  $T = T_c$ , one must have  $B = -p_c$  [15]. This provides a useful fixed point for extrapolations toward higher temperatures and indicates a possible form to describe  $B$  as a function of  $T$ :

$$B(T) = -p_c + \sum_{i=1}^n b_i [1 - (T/T_c)]^i \quad (21)$$

Table III. Experimental Density and Viscosity of Cyclohexane

$p$ (MPa)	$f_r$ (Hz)	$\gamma$ (Hz)	$\rho$ ( $\text{kg} \cdot \text{m}^{-3}$ )	$\eta$ ( $\text{mPa} \cdot \text{s}$ )
298.15 K				
0.10	1058.90	36.52	773.52	0.892
5.10	1057.05	37.70	778.13	0.942
10.10	1055.42	39.27	781.79	1.01
20.10	1052.25	42.15	789.16	1.14
30.10	1049.10	45.07	796.43	1.28
32.75	1048.34	45.86	798.07	1.32
308.16 K				
0.10	1062.65	33.11	764.16	0.752
10.13	1059.06	35.80	773.22	0.861
20.10	1055.83	38.35	781.21	0.969
30.10	1052.79	40.91	788.54	1.08
37.30	1050.46	42.95	794.07	1.18
323.15 K				
0.10	1067.93	29.21	750.24	0.605
10.15	1064.33	31.41	759.99	0.686
20.10	1061.01	33.60	768.76	0.770
30.10	1057.91	35.83	776.72	0.860
333.16 K				
0.10	1071.37	27.05	740.65	0.529
10.15	1067.69	29.04	750.97	0.598
20.10	1064.17	31.14	760.56	0.675
30.10	1061.11	33.25	768.52	0.756
38.00	1058.72	34.93	774.70	0.823
348.14 K				
0.10	1076.66	24.25	725.21	0.438
10.15	1072.61	26.12	737.00	0.498
20.20	1069.05	28.00	747.03	0.561
30.10	1065.76	29.98	755.97	0.632
38.00	1063.32	31.61	762.37	0.692

The parameters of Eq. (21) are also presented in Table VI, assuming the critical constants  $T_c = 533.4$  K and  $p_c = 4.02$  MPa [16]. The present set of results is represented by the Tait equation, using temperature-dependent  $\rho_0$  and  $B$  as given by Eqs. (20) and (21), with a precision of  $\pm 0.05\%$ .

Figure 2 contains a plot of the deviations of the present results at 0.1 MPa from their correlation using Eq. (20) and, also, the deviations of data from the literature: the values of IUPAC [12], one measurement by

Table IV. Parameters of the Tait Equation for Cyclohexane

$T$ (K)	$\rho_0$ ( $\text{kg} \cdot \text{m}^{-3}$ )	$B$ (MPa)	$C$	$\sigma$ (%)
298.15	773.52	76.72	0.200	0.02
308.16	764.16	69.27	0.200	0.03
323.15	750.24	62.44	0.200	0.01
333.16	740.65	57.48	0.200	0.02
348.14	725.21	50.15	0.200	0.01

Table V. Parameters of the Viscosity Correlation for Cyclohexane

$T$ (K)	$\eta_0$ ( $\text{mPa} \cdot \text{s}$ )	$D$ (MPa)	$E$	$\sigma$ (%)
298.15	0.892	354	4.45	0.3
308.16	0.752	132	1.80	0.3
323.15	0.605	151	1.94	0.0
333.16	0.529	212	2.69	0.1
348.14	0.438	342	4.35	0.1

Table VI. Coefficients of Eqs. (20), (21), and (22)

Cyclohexane; Eqs. (20) and (21)				
$d_0$ ( $\text{kg} \cdot \text{m}^{-3}$ )	$d_1$ ( $\text{kg} \cdot \text{m}^{-3} \cdot \text{K}^{-1}$ )	$10^3 d_2$ ( $\text{kg} \cdot \text{m}^{-3} \cdot \text{K}^{-2}$ )	$b_1$ (MPa)	$b_2$ (MPa)
907.42	-10.056	-1.4739	32.56	305.3
2,2,4-Trimethylpentane; Eq. (20)				
$d_0$ ( $\text{kg} \cdot \text{m}^{-3}$ )	$d_1$ ( $\text{kg} \cdot \text{m}^{-3} \cdot \text{K}^{-1}$ )	$10^3 d_2$ ( $\text{kg} \cdot \text{m}^{-3} \cdot \text{K}^{-2}$ )	$10^6 d_3$ ( $\text{kg} \cdot \text{m}^{-3} \cdot \text{K}^{-3}$ )	
1075.92	-2.4445	6.0227	-7.3492	
1,1,1,2-Tetrafluoroethane; Eq. (22)				
$d_1$	$d_2$	$\beta$		
1.93377	0.95348	0.3095		

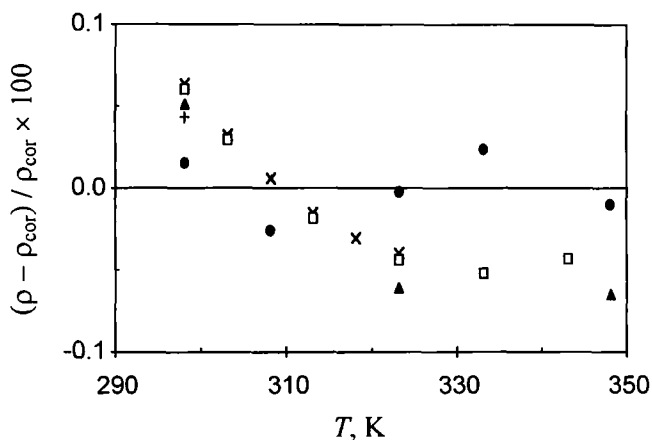


Fig. 2. Density of cyclohexane at 0.1 MPa: deviations of the present results and of literature data from Eq. (20). (x) Girard [12]; (+) R. Tanaka et al. [17]; ( $\Delta$ ) Y. Tanaka et al. [18]; ( $\square$ ) Vargaftik [19]; ( $\bullet$ ) present data.

R. Tanaka et al. [17], several others by Y. Tanaka et al. [18], and values tabulated by Vargaftik [19]. The measured density at 298.15 K and 0.1 MPa deviates less than 0.03% from the value obtained using the pycnometer for the same sample. The present results have a precision of  $\pm 0.03\%$  and no deviation of the literature values is greater than  $\pm 0.06\%$ .

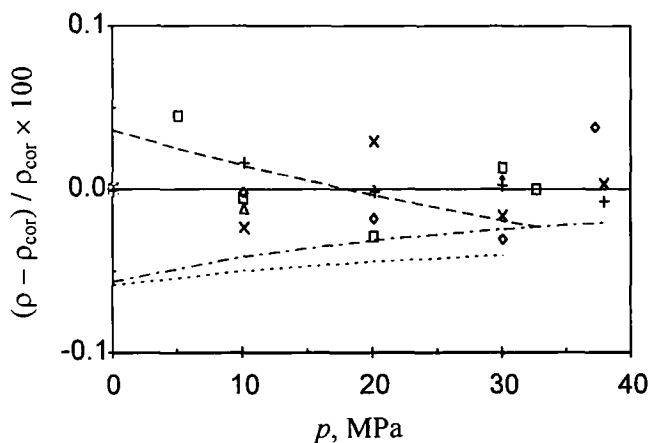


Fig. 3. Density of cyclohexane at high pressures: deviations of the present data (symbols) and of the correlation of Y. Tanaka et al. [18] (---, 298.15 K; - - -, 323.15 K; - · - ·, 348.15 K) from the Tait equation.



The present results of density and viscosity up to 38 MPa were compared to those of Y. Tanaka et al. [18]. Their densities at high pressure were measured using a piezometer, with initial values for each isotherm obtained with a vibrating-tube densimeter at 0.1 MPa. For the viscosities a torsional quartz-crystal instrument was used. The deviation plots can be seen in Figs. 3 and 4. The density deviations are never greater than  $\pm 0.06\%$  and the viscosity deviations are within  $\pm 1.5\%$ . Both are commensurate with the mutual uncertainties.

#### 5.4. 2,2,4-Trimethylpentane

The measurements in 2,2,4-trimethylpentane presented here were extracted from two large sets of data extending up to 100 MPa, one at temperatures from 298 to 348 K and the other from 198 to 298 K [2]. There was an interval of more than one year between the two sets of experiments, so their mutual agreement constitutes a good test of the reproducibility of the apparatus.

The present densities, taken at atmospheric pressure, are shown in Table VII. These data were correlated using Eq. (20), whose coefficients are presented in Table VI. The maximum deviations of the fit are of  $\pm 0.05\%$ .

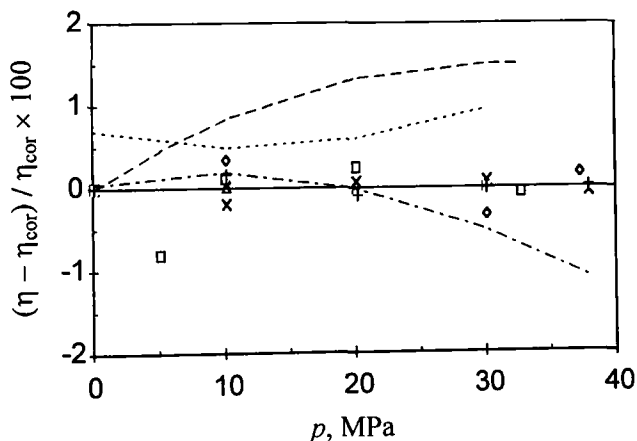


Fig. 4. Viscosity of cyclohexane at high pressures: deviations of the present data (symbols) and of the correlation of Y. Tanaka et al. [18] (---, 298.15 K; ·····, 323.15 K, - · - · - ·, 348.15 K) from the present correlation.

**Table VII.** Density and Viscosity of 2,2,4-Trimethylpentane at 0.1 MPa and of 1,1,1,2-Tetrafluoroethane at Saturation

2,2,4-Trimethylpentane			1,1,1,2-Tetrafluoroethane		
$T$ (K)	$\rho_0$ ( $\text{kg} \cdot \text{m}^{-3}$ )	$\eta_0$ ( $\text{mPa} \cdot \text{s}$ )	$T$ (K)	$\rho_{\text{sat}}$ ( $\text{kg} \cdot \text{m}^{-3}$ )	$\eta_{\text{sat}}$ ( $\text{mPa} \cdot \text{s}$ )
197.93	770.91	3.19	198.11	1511.3	1.10
222.91	749.32	1.58	223.05	1445.8	0.647
248.35	727.33	0.939	248.20	1372.4	0.401
273.15	707.72	0.650	273.15	1294.2	0.279
298.15	687.82	0.473	298.11	1206.6	0.205
298.15	687.87	0.474			
323.16	666.80	0.365			
348.16	644.75	0.289			

Two of the sets of data found in the literature were measured using vibrating-tube densimeters. Those of Dymond et al. [20] extend from 298.15 to 348.15 K; those of Malhotra and Woolf [15], from 298.15 to 323.15 K. The claimed accuracy for both these sets is  $\pm 0.1\%$ . The values recommended by IUPAC [12] were taken as another set. They extend from 293.15 to 323.25 K and are accurate within  $\pm 0.03\%$ . At low temperatures the only data found were those tabulated by Vargaftik [19] along the saturation line. Fortunately, the pressure difference between our results and the orthobaric line is small enough to render the error in the density insignificant, especially at these low temperatures.

A deviation plot of these density data from a correlation of the present results in the form of Eq. (20) is shown in Fig. 5. Only one point shows a deviation greater than  $\pm 0.1\%$ , this being the value from Vargaftik at the lowest temperature. There is an excellent agreement between the present measurements and those from IUPAC and also an agreement within the mutual uncertainty with all other sets.

The viscosities could only be compared at temperatures above 298.15 K with results from Dymond et al. [20], which have an accuracy of  $\pm 2\%$ . The deviations are  $-0.6\%$  at 298.15 K,  $-1.6\%$  at 323.15 K, and  $-2.5\%$  at 348.15 K, commensurate with the mutual uncertainty.

### 5.5. 1,1,1,2-Tetrafluoroethane

The set of results for HFC134a was also extracted from a wider set of measurements up to 100 MPa [2]. The ones reported here were obtained close to the saturation line, which is where literature data are available for

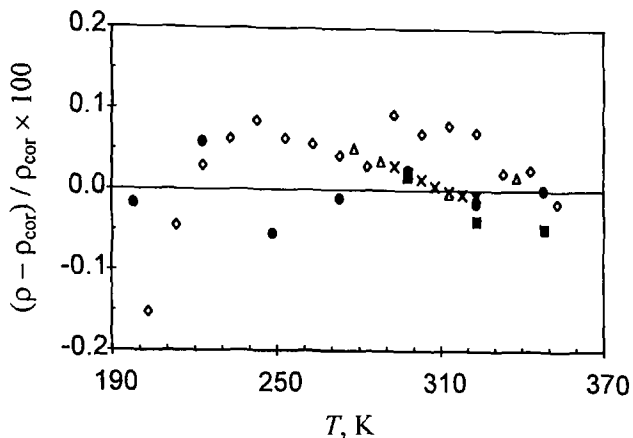


Fig. 5. Density of 2,2,4-trimethylpentane at 0.1 MPa: deviations of the present results and of literature data from Eq. (20). (×) Girard [12]; (△) Malhotra and Woolf [15]; (◇) Vargaftik [19]; (■) Dymond et al. [20]; (●) present data.

comparison. With the vibrating-wire densimeter the measurements could not take place exactly at saturation, owing to the possibility of formation of bubbles caused by the motion of the wire or even to the very slight heating resulting from the driving current. Therefore, the density data presented here were extrapolated to the orthobaric line using the Tait equation that correlates each of the isotherms measured [2]. The corrections applied were of the order of 0.02% at most.

The present saturated-liquid densities,  $\rho_{sat}$ , are shown in Table VII. They were correlated using an equation of the form

$$\rho_{sat}(T) = \rho_c(1 + d_1(1 - (T/T_c))^\beta + d_2(1 - (T/T_c))) \quad (22)$$

whose best-fit parameters are listed in Table VI. The critical temperature and critical density considered were 374.25 K and  $508 \text{ kg} \cdot \text{m}^{-3}$  [21]. The precision of the fit is better than  $\pm 0.03\%$ .

Figure 6 shows the deviations of the present data from the equation of state of Tillner-Roth and Baehr [21], which was adopted as a reference by the International Energy Agency. The maximum deviation observed is of  $\pm 0.1\%$ , which is the accuracy claimed for the equation of state. Original literature data were also included in the deviation plot. It is seen that the present results agree well with those of Basu and Wilson [22], which were measured by a flotation technique and should be the most accurate of all

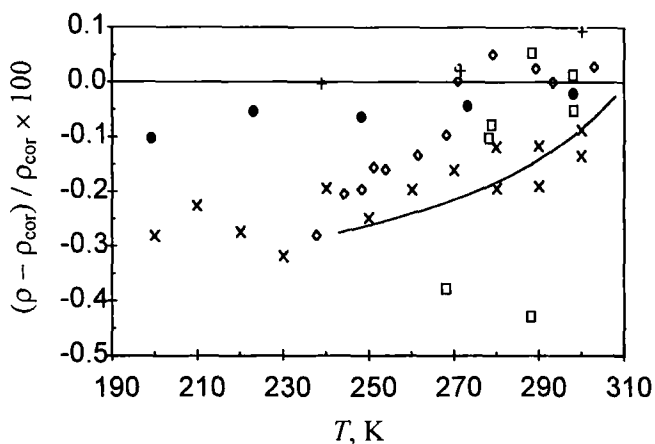


Fig. 6. Orthobaric liquid density of 1,1,1,2-tetrafluoroethane: deviations of the present results and of literature data from the EOS of Tillner-Roth and Baehr. (+) Basu and Wilson [22]; (x) Maezawa et al. [23]; (—) McLinden et al. [24]; (□) Morrison and Ward [25]; (◇) as in Oliveira and Wakeham [26]; (●) present data.

the literature data sets. Larger inconsistencies are observed for the densities of R134a than were for the other two liquids studied. Purity problems, which were known to exist for previous measurements with this refrigerant [13], are the likely cause for these errors.

The values for the viscosity at the two higher temperatures agree within the mutual uncertainties with those reported by Oliveira and Wakeham [26]—the deviations are of 2.5% at 298.11 K and of 2% at 273.15 K. The present value at 248.20 K shows a deviation of about 5% from the value of [26]. This deviation is larger than usual, but discrepancies among published viscosities of R134a reach about 30% in this range of conditions [26], so the accuracy is difficult to assess at this point. At lower temperatures no reliable data were found for comparison.

## 6. CONCLUSIONS

The three sets of measurements presented, which cover a range from 197 to 248 K and up to 40 MPa for three fluids, were all analyzed with the same set of cell parameters. All of these data agree with the best literature values within their mutual uncertainty, both in the density and in the viscosity. This shows that there is no apparent systematic error introduced by the fact that the cell parameters were obtained from one experiment in 2,2,4-trimethylpentane at room temperature and atmospheric pressure.

This observation is equivalent to the statement that the set of parameters would be identical within the precision if any other reference point had been used.

This conclusion reinforces the assertion that the theoretical model of the densimeter is complete and rigorous, and the measurements would be absolute in the metrological sense if the cell parameters could be determined precisely and accurately by independent, absolute means. As noted earlier, their determination from a reference experiment is a matter of choice here, and not the result of any fundamental deficiency.

A relevant characteristic of experimental methods described by rigorous models is that the accuracy should have values close to the precision, whereas in relative methods very high precisions can sometimes be attained, but the accuracies depend severely on the availability of high-quality calibrants over the whole ranges of experimental conditions.

It has been shown that simultaneous measurement of viscosities is possible and that the accuracy attained in this property is sufficient to guarantee a high accuracy in the calculated densities. This constitutes one further very stringent test both for the intrinsic quality of the theoretical model and for the adherence of the present apparatus to it.

The precision of the density measurements is  $\pm 0.03\%$  and their accuracy is estimated as  $\pm 0.05\%$ . The viscosities exhibit a precision of  $\pm 0.6\%$  and have an estimated accuracy of  $\pm 2\%$ .

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