A Vibrating-Tube Densimeter for Fluids at High Pressures and Temperatures[1]

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A vibrating U-tube apparatus has been developed for determining the densities of pure fluids and fluid mixtures at 10–200 MPa and 323–773 K. Measured parameters are P, T, and τ (period of vibration). Fluids are injected into the U-tube at constant P and T. Three or more reference fluids are used to calibrate the response of the instrument. Fluid mixtures are produced by pumping pure fluids into T-junctions on the upstream side of the U-tube using high accuracy syringe pumps. An automated syringe pump is used to maintain P at setpoint ± 0.01 MPa. T is controlled to ± 0.01 K using a closed-loop, electronic signal amplification/feedback system. For mixtures, a statistically significant number of measurements of τ are obtained to account for the effects of small heterogeneities in fluid composition (generally < 0.005 X_i). Typically, density data for 15 fluids can be obtained in a 6- to 8-h period. Considering all of the potential sources of error in the experimentation, conservative estimates of uncertainty are as follows: P, ± 0.02 MPa; T, ± 0.05 K; ρ (pure fluids), ± 0.0005 g·cm^{-3}; and ρ (fluid mixtures), $\pm 0.0005 - 0.0010$ g·cm^{-3}.

KEY WORDS: density; high pressures; high teperatures; syringe pumps; vibrating U-tube.

1. INTRODUCTION

Previous investigators [1–4] have shown that vibrating-tube apparatus can be used to obtain extremely accurate and precise data on the densities

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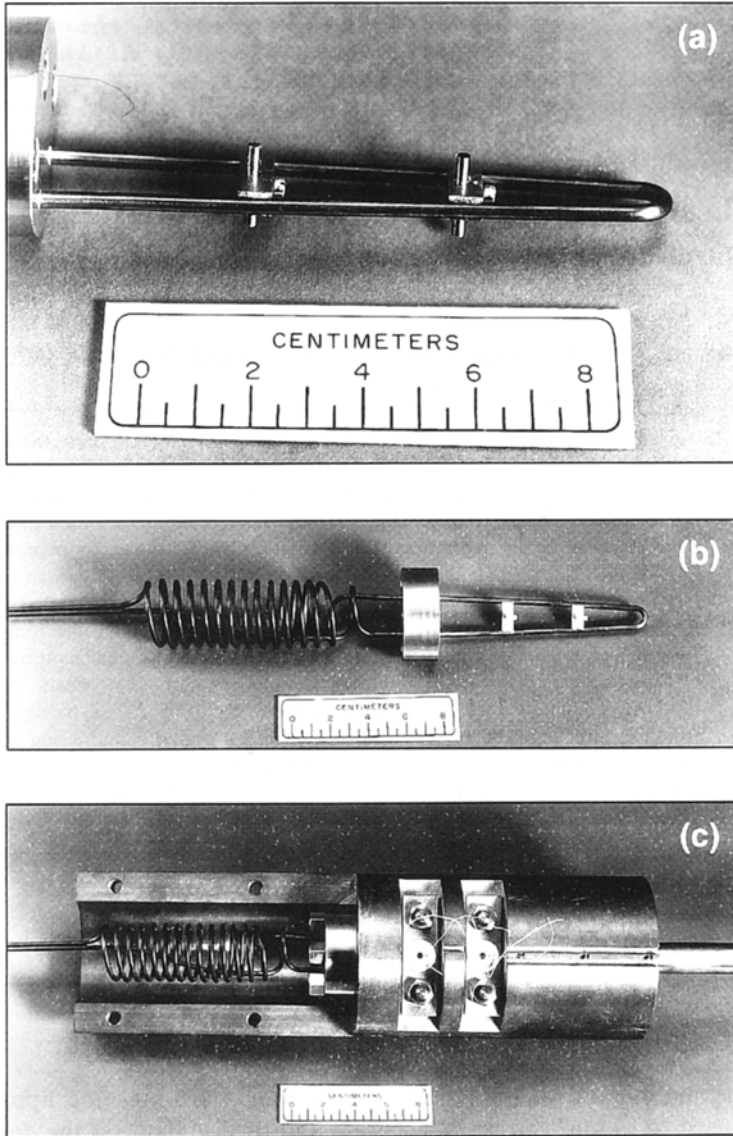
Fig. 1. Photographs of key parts of the U-tube assembly. (a) A closeup view of the U-tube and rod magnets ("drive" magnet on the left, "pickup" magnet on the right). (b) Photograph of the heat-exchange coils on the upstream and downstream sides of the U-tube (14 coils on the upstream side, 1 coil on the downstream side). These coils and the U-tube were fabricated

of many kinds of fluids at pressures up to 70 MPa and temperatures as high as 723 K. However, for numerous geologic applications, accurate information is needed on the densities of aqueous and carbonic fluids that form and circulate deep in the earth's crust, where $P \gg 70$ MPa. In this paper, we describe a high-pressure vibrating-tube densimeter (HPVTD) that can be used to measure the densities of low- to medium-viscosity fluids at pressures up to 200 MPa and temperatures as high as 773 K.

Numerous technical difficulties are encountered in designing and constructing a VTD for operation at $P > \sim 50$ MPa. One of the major problems is deformation of the U-tube. High internal pressure, high temperature, and frequent cycling of internal pressure and temperature over wide ranges cause the tube to expand inelastically at a variable and unpredictable rate. This is a severe difficulty, because the accuracy of the VTD method relies partly on the assumption that the internal volume of the U-tube remains constant while density data are being collected.

For our VTD experimentation, we adopted a three-part strategy to deal with difficulties associated with tube deformation and other causes of instrument drift. First, we use a thickwalled U-tube that has been heat-treated to a very high tensile strength. This enables VTD experimentation at pressures up to ~ 200 MPa and temperatures as high as 773 K with minimal inelastic expansion of the tube. Second, we obtain all of our density data at fixed $P-T$ conditions. This is done because, after a period of U-tube "conditioning" at a new set of $P-T$ conditions, the electronic signal from the tube (period of vibration, τ) becomes nearly constant, indicating

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from a single length of 0.3175-cm-O.D., 0.1588-cm-I.D. Inconel 718 tubing. The tubing is brazed to the tube holder located just above the centimeter scale. (c) Photograph of the U-tube assembly, partly assembled. The U-tube, heat-exchange coils, and electromagnets are attached to the support cylinder. In addition to affording rigid support for the detachable parts of the U-tube assembly, the support cylinder serves as a large thermal mass and a rapid heat conductor. Missing on the left is the clamshell cover for the cylinder (Fig. 2), which fits directly over the cavity that houses the heat-exchange coils. After the clamshell piece is attached to the top of the cylinder, (1) silver beads are poured into the heat-exchange cavity, and (2) two thin plates are screwed onto the end of the support cylinder to seal the silver beads inside the cavity. The silver beads provide additional thermal mass and increase thermal coupling between the support cylinder and the heat-exchange coils. Four two-conductor ceramowire leads (not shown) are used to energize the electromagnets. These leads fit into four longitudinal grooves in the support cylinder, two of which can be seen on the right-hand side of this photograph.

that all potential causes of instrument drift—including tube deforma-
tion—have been eliminated temporarily.[5] Third, we collect density data for
experimental and reference fluids in discrete (daily) 6- to 8-h experimental
sessions, and in each session, τ is measured repeatedly for one of the
reference fluids to check for instrument drift.

2. U-TUBE ASSEMBLY

The U-tube vibrates at ~ 160 Hz inside a U-tube assembly suspended
in a DC-powered resistance furnace (Figs. 1 and 2). Harmonic oscillation
of the tube is induced and measured by a Paar DMA 60 densimeter, via
magnetic coupling between two rod magnets attached to the U-tube
(Fig. 1a) and four electromagnets fastened to the support cylinder (Figs. 1c
and 2). To ensure steady, continuous harmonic oscillation of the U-tube,
the rod magnets and electromagnets are shielded from external magnetic
fields by a thin, electrically grounded, chrome-plated iron liner inside the
furnace; all detachable parts of the U-tube assembly are fastened tightly to
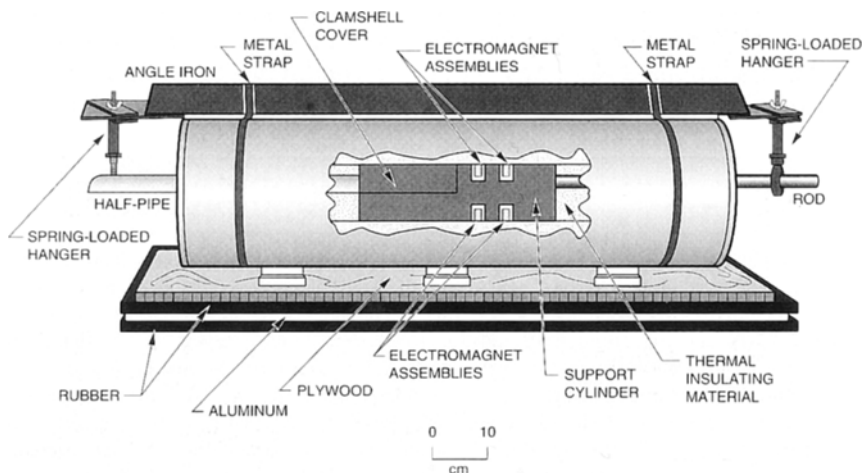the support cylinder; and the tubes and fittings immediately upstream and

Fig. 2. Schematic illustration of the U-tube assembly, the resistance furnace, and the
apparatus used to dampen external vibrations. During experimentation, the furnace is slowly
flushed with Ar to reduce oxidation of the copper-alloy support cylinder and the silver beads.

[5] After changing experimental P and/or T, we observe prolonged periods of time during which
τ drifts very rapidly, thus precluding collection of density data. This drift decreases
asymptotically with time, to the point where no significant change is detectable over a period
of 12–24 h.

downstream from the U-tube are clamped with brackets. Also, to dampen vibrations from external sources, the U-tube assembly is suspended from the ends of the furnace using spring-loaded hangers, and the furnace rests on two sheets of rubber padding separated by an aluminium plate (Fig. 2).
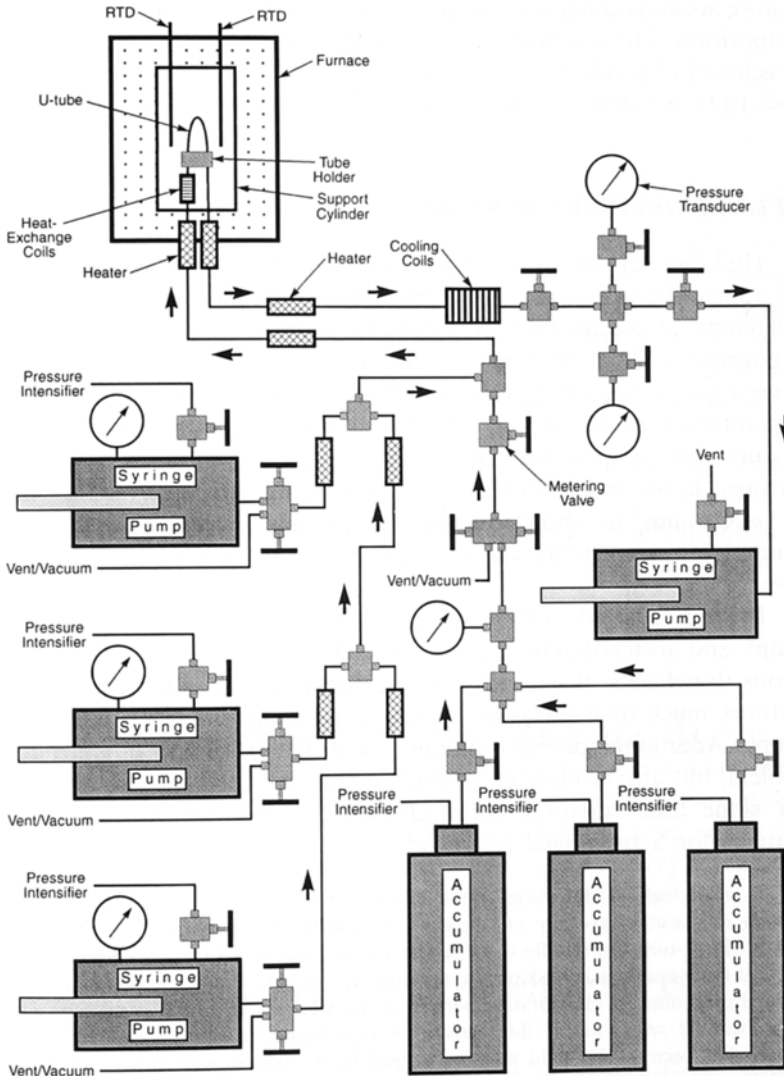

Fig. 3. Schematic diagram of the pressurized portion of the HPVTD.

3. PRESSURE INTENSIFICATION AND STORAGE OF
HIGH-PRESSURE FLUIDS

High pressure is generated by a gas booster and three syringe pumps on the upstream side of the U-tube (Fig. 3). High pressure fluids are stored in the barrels of the pumps and in three accumulators. Generally, the pumps are pressurized with fluids that are used to create fluid mixtures, because accurate pumping is required to create mixtures of precisely known composition. The accumulators are used to store reference fluids and are pressurized to levels well in excess of experimental pressure to permit the fluids to be injected into the U-tube by throttling through a metering valve.

4. FLUID DELIVERY SYSTEM

High-pressure fluids are delivered to the U-tube through T-junctions and a metering valve (Fig. 3). By injecting two or more pure fluids into the T-junctions at precise rates, it is possible to create single-phase and nearly homogeneous fluid mixtures of virtually any intermediate composition *during experimentation*. $\sum R_i$, where R_i is the rate of flow of a *pure* fluid i, is maintained at 40 $cm^3 \cdot h^{-1}$ to permit precise control of experimental pressure and temperature[6] and to promote mechanical mixing of fluid mixtures. R_i for the fluids in the delivery pumps are set by programming the electronics in these pumps. R_i for the reference fluids in the accumulators are established manually by throttling through the metering valve.

Prehomogenized fluid mixtures can be loaded into the fluid delivery pumps and metered into the U-tube, but this methodology has several serious drawbacks. If data are to be collected for a large number of fluid mixtures, much time and effort is spent pressurizing and depressurizing the pumps. Additional delivery pumps could be procured to alleviate this problem, but at considerable additional financial cost. Another difficulty is that some fluid mixtures become heterogeneous compositionally if left unstirred for a prolonged period of time. Finally, in many fluid systems,

[6] If $\sum R_i$ is too high, (1) the piston in the fluid recovery pump (Fig. 3) cannot retract rapidly enough to maintain pressure at setpoint ± 0.01 MPa (see Section 6); (2) fluid will flow toward the U-tube too rapidly to be heated to experimental temperature prior to entering the heat-exchange coils immediately upstream from the U-tube, thus perturbing steady-state thermal conditions in the vibrating portion of the VTD system; and (3) the fluid recovery pump will fill with "waste" fluid before an experimental session is complete, which is undesirable, because this fluid must be purged before experimentation can continue, and after interrupting operation of the fluid delivery pumps during an experimental session, steady-state flow conditions cannot always be regained immediately.

thermodynamic immiscibility severely restricts the range of compositions over which single-phase fluids are stable at room temperature.

To minimize "noise" in plateau values for τ (see Section 7), the stream of fluid flowing through the U-tube must be as homogeneous as possible. Generally, this is not a serious problem for binary and multicomponent fluids that are single-phase at room temperature. However, fluids that are two-phase (or multiphase) at room temperature are more difficult to homogenize. We have addressed this problem in four ways (Fig. 3). First, the pure fluids used to create the mixtures are heated to a hypersolvus temperature prior to mixing. Thus, the pure fluids are completely miscible when they first come into contact in a T-junction. Second, our fluid delivery apparatus is configured so that pure fluids flow into T-junctions from opposite directions. This creates turbulence in these zones, which promotes mechanical mixing and chemical homogenization. Third, heating devices downstream from the T-junctions ensure that the temperature of the fluid remains sufficiently high to preclude phase separation prior to flow into the U-tube. Fourth, mechanical mixing of fluid in the section of the fluid delivery system downstream from the T-junctions is promoted by (1) flowing the stream of fluid through a series of constrictions, small cavities, and sharp bends and (2) inserting small-gauge, coiled wires into the cavities along this flow path.

Finally, we wish to point out that the section of the fluid delivery system on the downstream side of the T-junctions has—by design—a very small internal volume, and a minimum number of "fluid hideouts," to ensure that fluid flowing through the U-tube is not contaminated to any detectable degree by fluid injected previously.

5. FLUID RECOVERY SYSTEM

The apparatus on the downstream side of the U-tube (Fig. 3) is used to collect and store spent experimental fluids, and to control and monitor experimental pressure. The fluid recovery manifold contains two pressure tranducers—one to control experimental pressure, the other to measure experimental pressure (see next section). The fluid recovery ("take up") syringe pump receives and stores all spent experimental fluids.

6. CONTROL AND MEASUREMENT OF PRESSURE AND TEMPERATURE

During experimentation, pressure is held continuously at setpoint ± 0.01 MPa by steadily retracting the piston in the take-up pump as fluid

flows through the U-tube. Pressure on the downstream side of the U-tube is sensed by a pressure transducer (Fig. 3) that outputs a 0 to 10-V signal to a 12-bit-resolution PID (proportional-integral-derivative) controller. This controller, in turn, emits a millivolt output signal to the take-up pump. The resulting control signal causes the pump piston to advance if experimental pressure is below setpoint, or to retract if experimental pressure is above setpoint. Pressure readings are taken from a second pressure transducer adjacent to the pressure-controlling transducer (Fig. 3).

Experimental temperature is controlled to ± 0.01 K by means of a closed-loop, electronic signal amplification/feedback system. The resistance of a 100-Ω platinum RTD (resistance temperature detector) is read by a programmable digital temperature indicator equipped with a 12-bit DAC (digital-to-analog converter) that outputs -4.095 to $+4.095$ V in 1-mV increments. At each experimental temperature, a $mV \cdot K^{-1}$ resolution and a zero offset (K) are selected so that the DAC outputs 50 mV when temperature is at setpoint. (At the finest output resolution, $1 \ mV = 0.001$ K.) The mV signal emitted by the DAC is sent to a 12-bit-input, 10-bit-output PID temperature controller. The controller, in turn, sends a millivolt signal to a DC power supply, which energizes the windings in the resistance furnace.

7. DATA ACQUISITION

A staged flow-through methodology is used to measure τ for pure fluids. A continuous flow-through methodology is used to measure τ for fluid mixtures. Typically, plateau values of τ are reached in 8–20 min (Fig. 4). Plateau values for mixtures are obscured slightly by low levels of random "noise" caused by small heterogeneities in fluid composition (generally $<0.005 \ X_i$); consequently, for these fluids, we obtain a statistically significant number of measurements (typically, $n = 100–400$) for τ at each P–T–X condition and take the mean value as the final value for τ.

It has been our experience that superior density data are obtained when $\sum R_i = 40 \ cm^3 \cdot h^{-1}$. When $\sum R_i$ is $<40 \ cm^3 \cdot h^{-1}$, values for τ oscillate slowly within a narrow range. As $\sum R_i$ is increased up to $40 \ cm^3 \cdot h^{-1}$, the wavelength of this oscillation decreases. When $\sum R_i$ is $>40 \ cm^3 \cdot h^{-1}$, the fluid in one of the delivery pumps is used up before an experimental session can be completed.

Usually the rate of fluid flow has no effect on τ. However, occasionally we observe a small, systematic difference between τ measured while fluid is flowing through the U-tube and τ measured after stopping fluid flow. In this circumstance, we apply a small correction to τ to account for the effect of fluid flow.
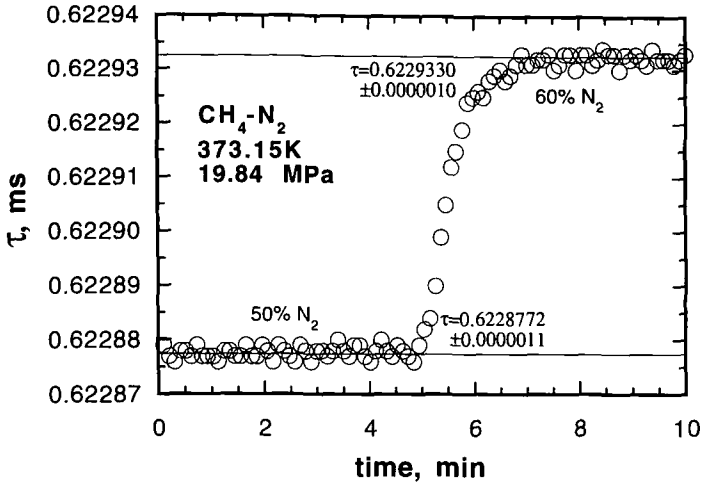
Fig. 4. Period of vibration (τ, ms) versus time (t, min) for a 10-min period during which a 40% CH_4–60% N_2 mixture was metered into the vibrating U-tube, replacing a 50% CH_4–50% N_2 mixture injected previously.

8. DATA REDUCTION

The fundamental equation for calculating densities of single-phase fluids by vibrating-tube densimetry is

$$\rho - \rho_0 = K(\tau^2 - \tau_0^2) \tag{1}$$

where ρ is the unknown density of a fluid, ρ_0 is the known density of a reference fluid (calculated from an equation of state), K is a parameter that depends on the mechanical properties of the vibrating tube, τ is the period of vibration of the U-tube when it is filled with the fluid of unknown density, and τ_0 is the period of vibration of the U-tube when it is filled with the reference fluid [1, 2]. If the U-tube behaves ideally at a fixed P and T, K is a constant, and Eq. (1) represents a linear relationship between τ^2 and ρ.

Figure 5 illustrates τ^2 vs ρ for three reference fluids (He, N_2, and Ar) and a series of CO_2–CH_4 mixtures. Values for τ were obtained from our HPVTD in a single experimental session. Densities for the three reference fluids were derived from published equations of state that have an estimated accuracy of $\pm 0.1\%$ [5, 6]. The straight line (Fig. 5) represents a linear least-squares fit to the data for the reference fluids. Numbers in parentheses are residuals, indicating the extent to which the values for τ^2
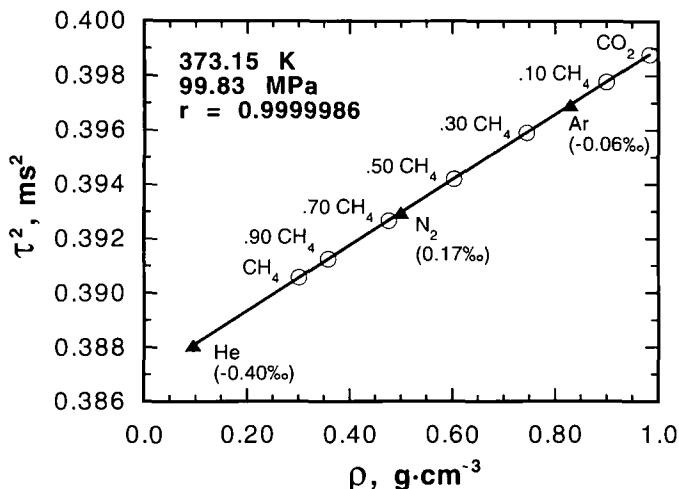
Fig. 5. Period of vibration squared (τ^2, ms^2) versus density (ρ, g · cm^{-3}) for three reference fluids (He, N$_2$, and Ar; filled triangles) and seven CO$_2$–CH$_4$ fluids (open circles).

deviate from the fitted line. These residuals, along with the correlation coefficient for the regression line (r = 0.9999986), show that the relationship between τ^2 and ρ is linear (i.e., the U-tube behaved ideally during the experimental session). Densities for pure CO$_2$, pure CH$_4$, and five CO$_2$–CH$_4$ mixtures (represented by open circles in Fig. 5) were determined by referencing values for τ^2 to the calibration line.

9. ACCURACY OF THE DENSITY DATA

Various experimental procedures and evaluation criteria are applied to ensure that the density data obtained from the HPVTD are highly accurate. Devices for controlling and measuring P and T are calibrated precisely on a regular basis. If instrumental drift is detected during an experimental session, all of the density data collected during that session are discarded. During each experimental session, data are collected for a minimum of three reference fluids to demonstrate conclusively that τ^2 vs ρ is linear. If any significant nonlinearity in τ^2 vs ρ is observed, the data collected during that session are discarded, and the session is repeated. From time to time, replicate experiments are performed to verify that remeasured densities are identical to original values within experimental uncertainty. We have also used our HPVTD to measure the densities of pure H$_2$O and pure CO$_2$ over wide ranges of P and T, thus permitting comparisons to be made between densities for these fluids determined

experimentally with our apparatus and corresponding densities calculated from the equations of state developed by Haar et al. [7] and Angus et al. [8]. The measured and calculated densities are fully accordant, considering the uncertainties associated with our experimental data ($\pm 0.0005 - 0.0010$ g $\cdot$ cm^{-3}) and the fitted equations ($\pm 0.1\%$ [7] and ± 0.1–0.5% [8].

Additional precautionary measures relate principally to the accuracy of density data for fluid *mixtures*. Our syringe pumps are calibrated precisely, and all pressurized components of the HPVTD are checked regularly for leaks. The densities of mixtures are measured at closely spaced P–T–X intervals; systematic variations in density with P, T, and X are to be expected and are observed. For ternary fluid systems, density data are collected along the three bisecting pseudobinary joins that cross at $X_i = X_j = X_k = 0.33$. Densities for this composition derived from the data for the three joins—collected during separate experimental sessions—must agree within experimental uncertainty; otherwise, densities for the fluids along one or more of the joins are remeasured. Following these procedures, we have obtained density data for CO_2–CH_4 and CO_2–N_2 mixtures at 10–60 MPa and 323–473 K. The P–T–X conditions of our experiments do not exactly match those explored by previous investigators [9–12], and to our knowledge previous investigators did not estimate uncertainties for density or molar volume; however, graphical examination and regression analysis indicate a high level of consistency among the various data sets.

ACKNOWLEDGMENTS

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