

A Continuously Weighed Pycnometer for Measuring Fluid Properties

W. R. Lau, C.-A. Hwang, H. B. Brugge, G. A. Iglesias-Silva,[†] H. A. Duarte-Garza, W. J. Rogers, K. R. Hall,* and J. C. Holste

Chemical Engineering Department, Texas A&M University, College Station, Texas 77843-3122

B. E. Gammon and K. N. Marsh[‡]

Thermodynamics Research Center, The Texas A&M University System, College Station, Texas 77843-3111

This paper documents the construction details and experimental procedures for the continuously weighed pycnometer used in our laboratory to measure fluid properties such as densities, saturation pressures, phase boundaries, and isothermal compressibilities. This apparatus consists of a cell suspended from an electronic balance at all times and a variable volume bellows cell which is used to adjust the confined sample density within an isothermal enclosure. The principal advantages of this apparatus are rapid measurement and relatively high accuracy. Some experimental results are presented to illustrate capability. The accessible experimental ranges are 100–450 K up to 200 MPa; measurement accuracy is 0.1% or better.

Introduction

Accurate information about the properties of fluid mixtures are important to industry for efficient operation of existing plants, design of new plants, production of fluid products, and efficient and profitable exploitation of natural resources. Industry faces a paucity of data on the properties of pure fluids and fluid mixtures. From the standpoint of processing and separation operations, the most important properties are vapor–liquid equilibrium (VLE) and volumetric (PVT) data.

This paper presents the design details for a continuously-weighted pycnometer capable of measuring a variety of fluid properties. Density measurements for either pure fluids or mixtures are possible which cover wide ranges of temperature and pressure. Saturation pressures of fluids can be determined. At phase boundaries, the changes in slope of the pressure *versus* change in sample volume are observable at the interface between a single-phase region and a two-phase region. Also, the isothermal compressibility is available from isothermal density measurements as a function of pressure.

Existing methods for measuring accurate densities often have limited temperature and/or pressure ranges. Some of the methods are also complicated and laborious. The apparatus described here provides rapid and accurate measurements. An average time for a density measurement is 20 min. The precision of the apparatus is better than 0.03 kg·m⁻³ which leads to relative precisions of 0.003% for liquids and 0.03% for gases with densities of 100 kg·m⁻³ or greater.

Density Measurement Methods

Several established experimental techniques exist for measuring fluid densities. Some methods measure the mass and volume of a sample, while others measure the

mass of a fixed volume of sample. Some methods do not require measurement of mass or volume but determine densities through measurements of other physical properties. Existing methods for density measurement fall into six major categories.

Mechanical Oscillator. This method measures the resonant frequency of a constant volume, mechanical-bending type oscillator that is filled with the sample as reported by Kratky *et al.* (1973), Leopold *et al.* (1977), and Albert and Wood (1984). The mass of the sample influences the frequency of oscillation which can be used to calculate the sample density. Such devices are commercially available, and they are especially convenient for fluids with suspensions such as those in the human body. However, density values must be interpolated between measurements of two standard fluids.

Burnett Method. Burnett (1936) proposed a method which does not require measurement of sample mass or volume. Instead, sample pressure is measured following each of a series of successive expansions at constant temperature. If the volume ratio for each expansion is constant, the sample densities are available using a special data-reduction technique. A major disadvantage is the wide spacing of data at high pressures.

Gasometer. Goodwin (1961) has described this method in detail. The apparatus consists of a constant volume cell from which the sample expands into a much larger predetermined volume. Sample mass is calculated from known density data or a correlation at the lower pressure. The major disadvantage is that the density of the expanded volume must be known or determined by other means. Also, the difficulty of maintaining a large volume at constant temperature usually results in larger uncertainties in the measured values.

Buoyancy Force Technique. This technique makes use of the Archimedes buoyancy principle in which the upward force on a sinker of known volume is directly proportional to the fluid density. The sinker which is a part of a sealed system containing the sample can be suspended from a balance as suggested by Reding (1965), Grigor and Steele (1966), Bowman and Schoonover (1967),

[†] Present address: Departamento Ingenieria Quimica, Instituto Tecnológico de Celaya, Celaya, Gto., Mexico.

[‡] Present address: Department of Chemical and Process Engineering, University of Canterbury, Private Bag 4800, Christchurch, New Zealand.

and Goldman and Scrase (1969). This arrangement becomes impractical for high-pressure or corrosive samples. An alternative is to suspend a magnetic sinker by magnetic force generated by an inductive coil as suggested by Hales (1970), Haynes (1976), and Masui *et al.* (1981). Because no physical attachment exists between the sinker and the weighing device, the sinker and the sample can be sealed from the rest of the apparatus. This technique can be used for very accurate measurements but is effective only for dense fluids. Kleinrahm and Wagner (1986) have proposed a technique in which the sinker floats in the sample and is weighed by a balance which is coupled magnetically to the sinker. The magnetic coupling device is an ingenious advance and makes their apparatus among the most precise and accurate ever.

Pycnometer and Dilatometer. Beattie (1934), Douslin *et al.* (1969), Shraiber and Kukolenko (1965), and Shana'a and Canfield (1966) have described various pycnometers and dilatometers. Each apparatus generally consists of a sample container (pycnometer) with a relatively long and narrow opening. Usually, the mass of the sample is determined by weighing, while the sample volume is determined by calibration or by measuring the mass of mercury which overflows from the pycnometer. The simpler pycnometers and dilatometers usually are restricted to limited temperature and pressure. Although the Beattie apparatus adopted by Douslin *et al.* (1969) can be used at higher pressures and temperatures, its complexity requires considerable experimental skill and experience.

Continuously Weighed Pycnometer. The major component of this apparatus is a constant volume pycnometer suspended continuously from a balance as described by Van Witzenburg and Stryland (1967) and Machado and Streett (1981). The pycnometer is filled and evacuated through a long and flexible capillary tube that remains attached to the pycnometer during weighing. This arrangement enables faster measurements and reduces handling errors. However, the accuracy of the mechanical beam balance used by Van Witzenburg and Stryland (1967) is reduced because of the restoring force induced on the feed tube by the vertical displacement of the balance pan. Machado and Streett (1981) use an electronic balance that has little vertical displacement and has an accuracy of 0.02 g which results in an $0.0006 \text{ g}\cdot\text{cm}^{-3}$ overall accuracy in their density measurements. However, their long feed tube exposes part of the sample to ambient temperature, and the air-filled isothermal bath inhibits low-temperature measurements because of possible condensation.

This paper describes an apparatus that employs the continuous weighing technique for fluid density measurements which are accurate to $0.0001 \text{ g}\cdot\text{cm}^{-3}$. The rate of data collection is one measurement every 20 min along an isotherm. Density measurements can be performed on gases, liquids, pure components, or mixtures at temperatures from 100 to 450 K and pressures up to 200 MPa although pressures transducers selected for convenience only permit measurements up to 70 MPa.

Experimental Theory

The current apparatus determines fluid density by using an electronic balance to measure the weight of a sample cell. From this weight measurement, the mass of the cell and its contents is:

$$m = (w + f)/g \quad (1)$$

where m is the mass of the cell, w is the apparent weight of the cell, f is the buoyant force exerted on the cell, and g is the local gravitational acceleration. The buoyant force

can be evaluated from the external volume of the cell and the density of the bath fluid surrounding the cell using the relationship

$$f = vdg \quad (2)$$

where d is the bath fluid density and v is the external volume of the cell. Substitution of eq 2 into eq 1 yields

$$m = w/g + vd \quad (3)$$

Assuming the local gravitational acceleration is constant over the duration of the experiment, eq 3 for the evacuated sample cell (denoted by the subscript e) becomes

$$m_e = w_e/g + v_e d_e \quad (4)$$

Similarly, eq 3 for the filled sample cell (denoted by the subscript f) is

$$m_f = w_f/g + v_f d_f \quad (5)$$

Because the sample mass, m_s , is the difference between the masses of the filled and evacuated sample cell, it is

$$m_s = m_f - m_e = (w_f - w_e)/g + (v_f d_f - v_e d_e) \quad (6)$$

If the bath fluid density remains constant during the measurement, the pertinent relationships are

$$d_f = d_e = d \quad (7)$$

and

$$m_s = (w_f - w_e)/g + (v_f - v_e)d \quad (8)$$

The sample cell expands by less than 0.02 cm^3 when filled to a pressure of 70 MPa; therefore, the buoyant force variation in eq 8 is negligible compared to the sample weight (approximately 10 g). Thus, eq 8 simplifies to

$$m_s = (w_f - w_e)/g \quad (9)$$

and the sample density is

$$\rho_s = m_s/V = (w_f - w_e)/(gV) \quad (10)$$

where ρ and V are the sample density and volume respectively. For calibration of the sample cell volume, eq 10 is

$$V = (w_f^{\text{cal}} - w_e^{\text{cal}})/g\rho_{\text{cal}} \quad (11)$$

where ρ_{cal} is the density of a calibration fluid. Substitution of eq 11 into eq 10 produces

$$\rho = \rho_{\text{cal}} \frac{w_f - w_e}{w_f^{\text{cal}} - w_e^{\text{cal}}} \quad (12)$$

As a result, the experiment does not depend upon accurate knowledge of g , the local acceleration of gravity, but only upon knowledge of the density of the fluid used for the volume calibration.

Apparatus

The continuously weighed pycnometer described here, which consists of a weight measurement system, an isothermal bath with a temperature control and measurement system, a sample pressurizing system, and a high-vacuum system, has been discussed in detail by Lau (1986). While the apparatus is similar to that of Machado and

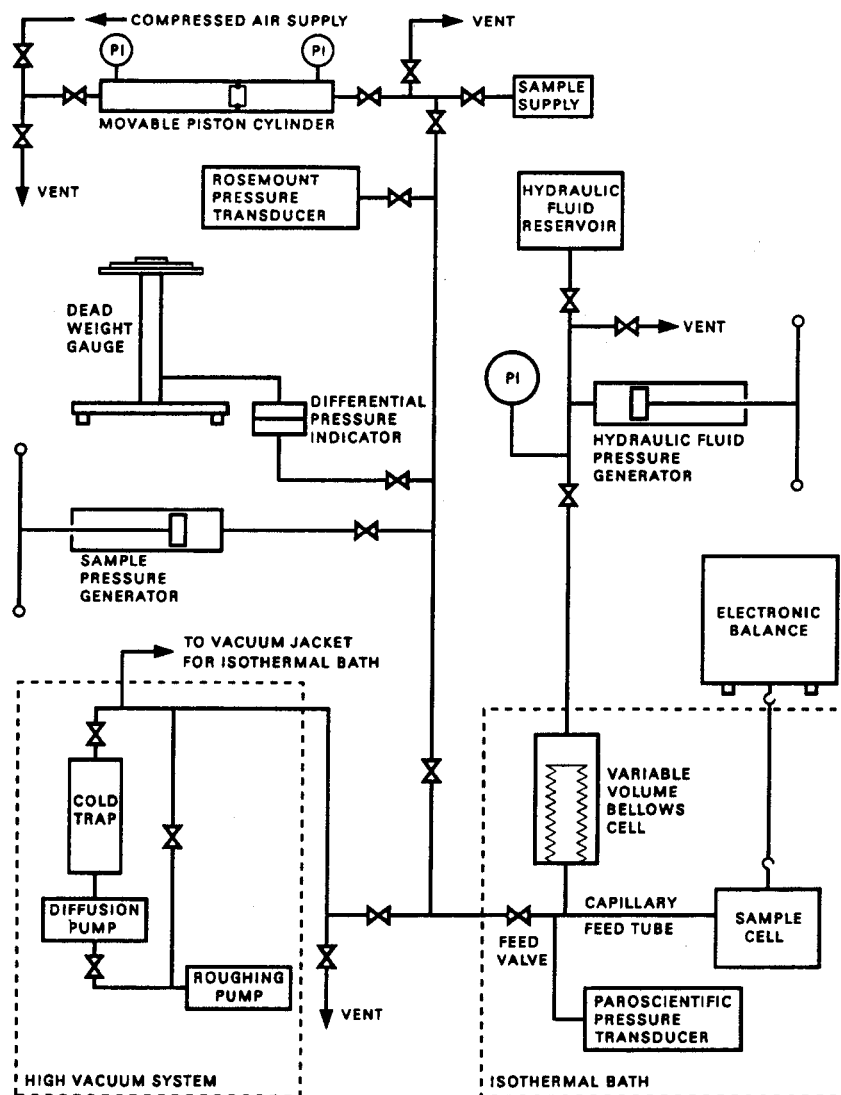


Figure 1. Overall schematic of the apparatus.

Streett (1983), it differs in the configuration of the balance, the pycnometer and flexible capillary feed line, the variable volume bellows cell and feed valve, and the design of the isothermal bath. The mass is determined with an electronic force balance; hence, the weighing pan has virtually no vertical displacement during the weighing operation, and the capillary feed line can remain attached to the pycnometer without affecting the weight measurement. The feed valve, placed inside the isothermal bath, confines the entire sample to the uniform temperature. The variable volume bellows cell, also within the thermostat, allows adjustment of the volume without transferring mass into or out of the isothermal region.

Figure 1 is a schematic of the apparatus, while Figure 2 shows the cross-sectional diagram of the isothermal bath and the balance chamber. The pycnometer (sample cell) hangs from the electronic balance by a wire which passes through a connecting tube into the isothermal bath. This connecting tube has a small diameter and a thin wall to minimize heat transfer from the isothermal bath to the balance chamber. The pycnometer material is beryllium copper (Be-Cu 175) which has high thermal conductivity and good mechanical strength. High thermal conductivity reduces temperature gradients across the sample cell, while good mechanical strength is needed for high sample pressures. The outside and inside diameters of this sample cell are 27 and 16 mm, respectively. This sample cell has been

tested successfully to a pressure of 340 MPa at room temperature. Figure 3 is a cross section of the sample cell. A calibration fluid, for which accurate density data exist, is used to establish the cell volume as well as its pressure and temperature dependence. The pycnometer is filled and evacuated through a straight, stainless-steel capillary that remains attached to the pycnometer without affecting the precision of the balance. The balance and the pycnometer are immersed in helium at a pressure controlled to minimize changes in buoyancy (helium has a high thermal conductivity and a low density). Densities are determined from the measured masses and the known volume of the pycnometer.

The isothermal bath consists of two temperature-controlled copper compartments connected by a short copper tube. The pycnometer is inside one compartment, while the feed valve, variable volume bellows cell, and a pressure transducer are in the other compartment. A feed valve allows the entire confined sample to be within the same uniform temperature which is important when the fluid exists as one phase at room temperature and as a different phase at the measurement temperature. A variable volume bellows cell shown in Figure 4 allows adjustment of the overall density even when the feed valve is closed. The isothermal bath is inside a temperature-controlled, aluminum radiation shield as well as a vacuum chamber to minimize heat transfer. This shield further

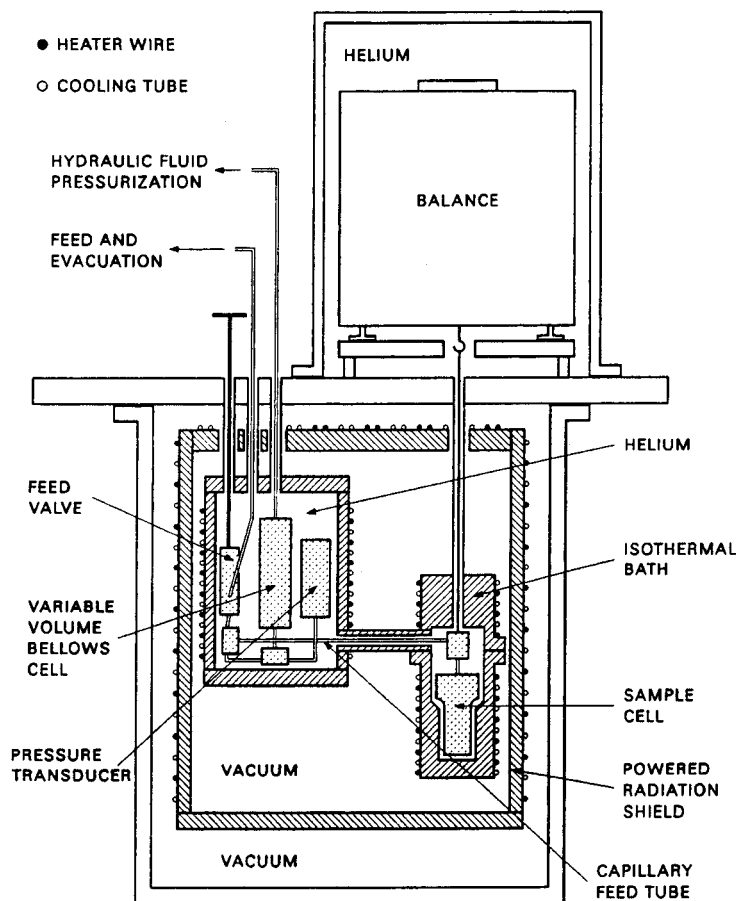


Figure 2. Cross section of isothermal bath and balance chamber.

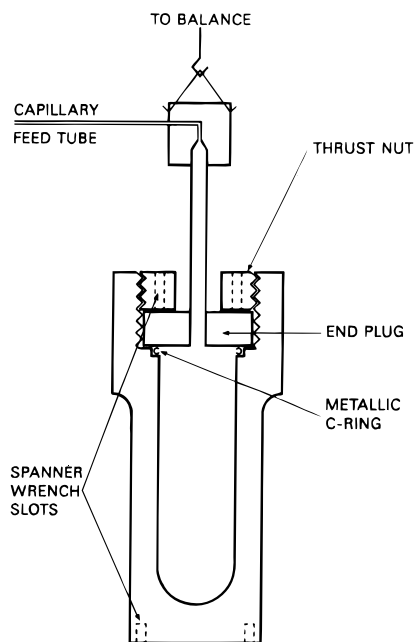


Figure 3. Cross section of the sample cell.

decreases the heat loss from the isothermal chamber and improves the uniformity of the sample temperature. A manual switch selects either high or low voltage levels for the heaters for the isothermal bath and the radiation shield. The high voltage level (fixed at 220 VAC) provides a sweep rate of $3 \text{ K}\cdot\text{min}^{-1}$ and is used to change from one temperature setting to another. The low voltage level (variable from 0 to 30 VAC by manual control) is used to

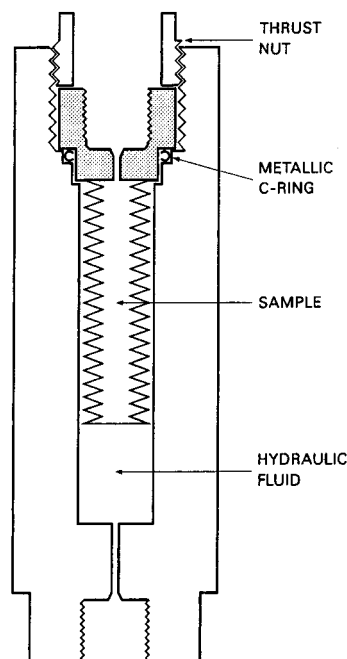


Figure 4. Cross section of the variable-volume bellows cell.

control the bath and shield temperatures at selected fixed values.

The balance (Arbor Laboratories model 507) has a completely electronic mechanism, a capacity of 500 g, and a precision of 0.1 mg and incurs vertical displacements less than $1 \mu\text{m}$ during the weighing operation. This $1 \mu\text{m}$ vertical displacement of the pycnometer cell creates a very small restoring force which is the reason the capillary feed line may remain attached during the mass measurement.

The balance is contained within a chamber with 13 mm thick aluminum walls to withstand atmospheric pressure when the chamber is evacuated before filling with helium. Elimination of the buoyant force effects requires that the bath fluid density remain constant throughout the experiment. To achieve $\pm 0.0001 \text{ gm}\cdot\text{cm}^{-3}$ requires that the helium pressure be constant within $\pm 1\%$. The chamber operates at a pressure near atmospheric, so the pressure tolerance is approximately $\pm 2 \text{ kPa}$. For gases heavier than helium, the pressure control requirement would be much more stringent.

A flexible, 316 stainless steel capillary tube connects the cell to a tee, which in turn is connected to the pressure indicator, sample pressurizing system, and through a valve to the external feed and vacuum manifold. This capillary has a length of 200 mm and an outside diameter of 0.8 mm. Simulating the cell acting on the capillary as a point load at the end of a cantilever beam, a $1 \mu\text{m}$ vertical displacement of the cell creates a restoring force of 0.045 mg, which is less than the precision of the balance.

Pressure measurements above 1.4 MPa utilize either a Rosemount (model 1333G10) strain gauge pressure transducer operated at room temperature or a Paroscientific (model 700) Digiquartz pressure transducer located in the isothermal bath. Pressures below 1.4 MPa are measured with a Ruska (type XR-38) pressure counter employing a fused quartz bourdon tube (room temperature) or a T-Hydrionics (model TH-1) pressure transducer (bath temperature). All the pressure devices are calibrated against a DH Instruments (type 26000) automatic pressure standard (dead-weight gauge, DWG).

Temperatures are measured with a MINCO four-lead platinum resistance thermometer (PRT, model S1059PA5 \times 10), which is adjacent to the pycnometer on the inside surface of the compartment housing the pycnometer. Initial measurements with differential thermocouples showed that the temperature gradients between the ends of the sample cell are less than 3 mK and that the difference between the temperature of the sample cell and that measured by the thermometer is less than 5 mK. The thermocouples then were removed to avoid introducing spurious forces to the cell.

Experimental Procedures

Density. The general procedure for density measurements along an isotherm follows. After the predetermined temperature of the isothermal bath containing the evacuated cell is established, the balance is tared and a fixed known mass is added to calibrate the balance. Next, the valve connected to the fluid supply is opened to fill a movable piston cylinder (MPC), and the fluid is compressed to 13.5 MPa (limit of the MPC) by introducing compressed nitrogen to the opposite side of the MPC. The fluid then is further pressurized with either a sample fluid pressure generator or a hydraulic fluid pressure generator. When the fluid temperature stabilizes at the controlled temperature, the pressure and balance readings are recorded. Density measurements are made at a series of decreasing pressures. The pressure can be adjusted by the pressure generator, by the variable volume bellows cell, or by venting part of the fluid.

If a two-phase region is encountered during an isothermal filling process, the pressure must be increased above the cricondenbar at a temperature above the cricondenbar to ensure that the sample remains homogeneous. The temperature is then lowered to the desired temperature while fluid is added continuously to maintain the pressure above the cricondenbar. In these cases, density

measurements before and after pressurizing the fluid must be made to verify homogeneity and to test the repeatability of the pressure transducers. In addition, the mass of the evacuated pycnometer cell and the zero readings of the pressure transducers are recorded after the isothermal run.

Saturation Pressure. Saturation pressures are determined after completing density measurements for each isotherm. The variable volume bellows cell is expanded to permit a vapor bubble of about 1 cm^3 to form in the presence of about 12 cm^3 of liquid within the pycnometer and bellows cell. The vapor bubble volume could vary while determining the saturation pressures. To promote nucleation for every isotherm, the liquid is expanded metastably to pressures below the vapor pressure of the fluid and the vapor bubble is formed by cycling the pressure in this metastable region or the feed valve is opened and closed. During the pressure cycling, metastable states are observed (including negative pressures in some cases).

Phase Boundary. Measurements on mixtures have shown that it is possible to detect phase boundaries with this apparatus. The strokes of the hydraulic fluid pressure generator used to adjust the volume of the bellows cell are carefully recorded. These volume changes of the bellows cell, which are proportional to the movement of the stroke of the pressure generator, result in change of the overall sample volume. An abrupt change in the slope of pressure versus change in sample volume occurs in the vicinity of the phase boundary. In most cases a metastable state is observed before a vapor bubble forms. The changes are confirmed by observations of changes in slope of the measured densities.

Isothermal Compressibility. Because measurements occur along isotherms, the density–pressure relationship can provide the isothermal compressibility, β_T :

$$\beta_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (13)$$

For liquids, the density can be expressed as a function of pressure:

$$\rho = \sum_{i=0}^n a_i P^i \quad (14)$$

Usually two terms are sufficient to fit the data satisfactorily, and the isothermal compressibility can be calculated analytically. The isothermal compressibility also can be determined graphically. From eq 1

$$\ln \left(\frac{V}{V_0} \right) = -\beta(P - P_0) \quad (15)$$

where V and V_0 are molar volume at P and P_0 , respectively. Because the variation of the molar volume with pressure for liquids is small

$$\ln \left(\frac{V}{V_0} \right) = \ln \left(\frac{V - V_0}{V_0} + 1 \right) \approx \frac{V - V_0}{V_0} \quad (16)$$

Substituting eq 16 into eq 15 yields

$$\frac{V_0 - V}{V_0} = \beta_T(P - P_0) \quad (17)$$

Equation 17 indicates that, for any liquid, the slope of a

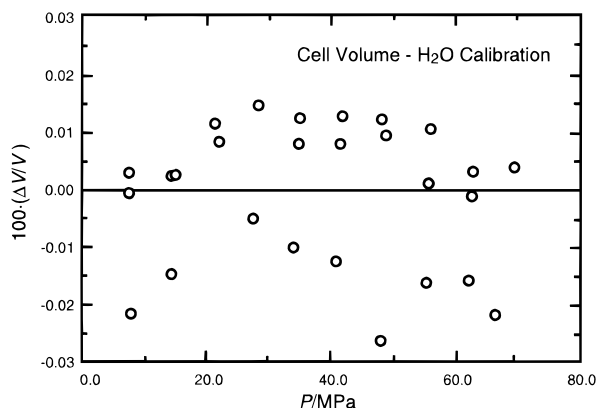


Figure 5. Deviation of sample cell volume from eq 12.

plot of $(V_0 - V)/V_0$ as a function of $P - P_0$, is the isothermal compressibility.

Results

The sample density, ρ_s , at P, T results from dividing the measured mass of the sample, m_s , in the cell by the known cell volume:

$$\rho_s(P, T) = \frac{m_s}{V(P, T)} \quad (18)$$

Water was used as the calibration fluid to determine the effective sample volume, which is the volume of the sample that contributes to the weight change measured by the balance. Because the sample inside the capillary acts as a uniform load on a beam supported at two ends, the effective sample volume equals the sample cell volume plus approximately one-half of the capillary volume. The volume calibration was performed at temperatures between 300 K and 450 K, with increments of 50 K, up to 68 MPa. The cell volume was determined from eq 11 and water density values reported by Kell (1975). The extrapolation of eq 19 below 300 K was confirmed to be accurate by measuring densities for carbon dioxide and comparing the results with the equation of Setzmann and Wagner (1991), which is based upon the accurate experimental results reported by Duschek *et al.* (1990).

The temperature and pressure dependence of the sample cell volume is represented well by

$$V = V_0 \exp[\alpha_1(T - 300) + \alpha_2(T - 300)^2 + \alpha_3P] \quad (19)$$

where V and V_0 have units of cm^3 , T is in K, P is in MPa, and the α_i are fit parameters. Figure 5 shows the deviations of the measured volumes from eq 18 (the average deviation is 0.01%). The measured volumes compared to values predicted by thermal expansion coefficient and elasticity modulus of Be-Cu 175 present an average deviation of 0.017% (the main contribution being the temperature effect). This effect may be caused by the precipitation of the alloy at higher temperatures.

The uncertainties in the pycnometer density measurements arise from cell volume calibration and mass determinations. The error in the cell volume calibration (which includes random errors introduced by temperature and pressure measurements, calibration fluid properties uncertainties) is about 0.04% and the mass determinations are valid within 1 mg, indicating stability of the tare weight. The estimated accuracy of the density measurements (95% confidence limits) is

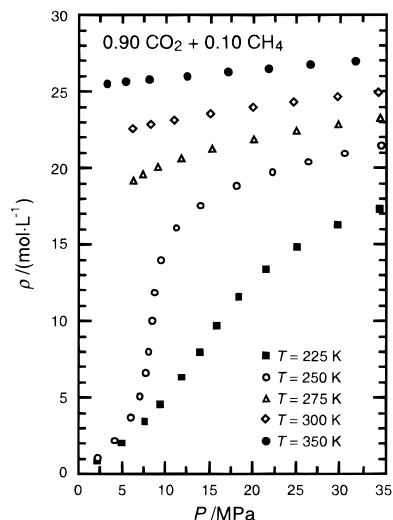


Figure 6. Density-pressure diagram for CO_2 (90 mol %) + CH_4 (10 mol %) mixture. The data appear in Hwang *et al.* (1995).

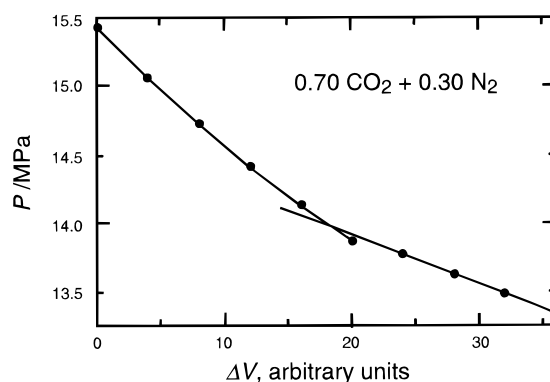


Figure 7. Observed behavior for CO_2 (70 mol %) + N_2 (30 mol %) mixture at 245 K in the vicinity of the phase boundary. The data appear in Duarte-Garza *et al.* (1995).

$$\frac{\Delta\rho}{\rho} = \left\{ \left(\frac{0.15}{\rho} \right)^2 + 1.6 \times 10^{-7} \right\}^{0.5} \quad (20)$$

where ρ has units of $\text{kg}\cdot\text{m}^{-3}$.

The results presented here illustrate the capabilities of the instrument. Figure 6 presents the experimental densities of a nominal mixture containing 90 mol % CO_2 and 10 mol % CH_4 . At low temperatures, the mixture exhibits liquidlike behavior (low compressibility). The transition from liquidlike behavior to gaslike behavior is extremely sharp and is readily apparent in the vicinity of the critical temperature (approximately 300 K). It is in this region that most equations of state have difficulty representing experimental results. The liquid and gaseous regions become less distinctive at about 350 K.

Figure 7 demonstrates determination of a saturation boundary point for a nominal 70 mol % CO_2 + 30 mol % N_2 mixture (or a vapor pressure for a pure component). The higher pressure points are single phase, and the lower pressure points are two phase (note, however, that one metastable state was observed). The phase boundary determination is accurate to about 0.05 K and 0.01% in pressure, but these limits depend upon the region of the phase boundary to some degree.

Figure 8 is a plot of relative volume against pressure and the slope gives the isothermal compressibility for a 2-methyl-2-propanol (95 wt %) + water (5 wt %) mixture. The linearity of the slope indicates that β_T is independent of pressure over the range measured. The uncertainties in ΔV and ΔP are $0.05 \text{ kg}\cdot\text{m}^{-3}$ and 0.003 MPa respectively.

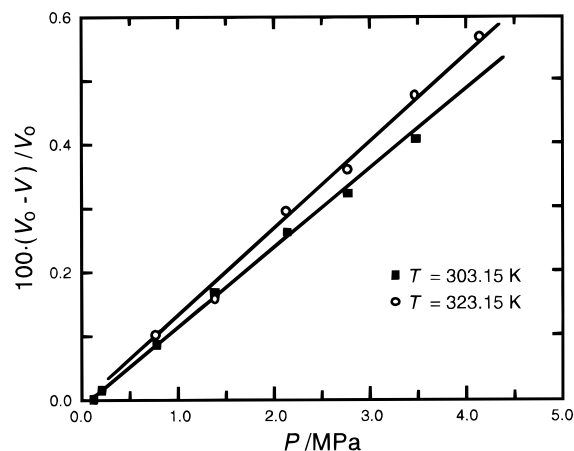


Figure 8. Relative volume against pressure for 2-methyl-2-propanol (95 wt %) + water (5 wt %) mixture.

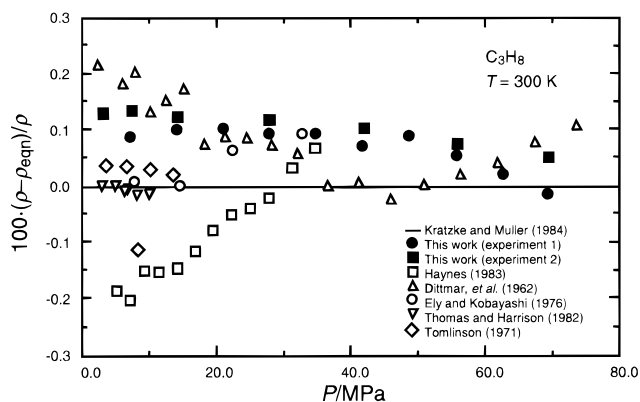


Figure 9. Relative deviations of measured propane densities at 300 K from the equation of Kratzke and Muller (1984).

Figure 9 demonstrates measurements on propane at 300 K. The reproducibility of the pycnometer data is 0.03%. The relative deviations of our measurements and other reported values are relative to an equation of state reported by Kratzke and Muller (1984). Our results at 300 K agree well with values reported by Ely and Kobayashi (1978), Thomas and Harrison (1982), and Tomlinson (1971). A discrepancy of up to 0.2% exists between our results and values reported by Haynes (1983) at lower pressures, but the agreement improves with increasing pressure, and the discrepancy is less than 0.01% at the maximum pressure of 40 MPa.

Literature Cited

- Albert, H. J.; Wood, R. H. High-precision Flow Densimeter for Fluids at Temperatures to 700 K and Pressures to 40 MPa. *Rev. Sci. Instrum.* **1984**, *55* (4), 589.
- Beattie, J. A. An Apparatus and Method Used for the Measurement of the Compressibility of Several Gases in the Range of 0 °C to 325 °C. *Proc. Am. Acad. Arts Sci.* **1934**, *69*, 389.
- Bowman, H. A.; Schoonover, R. M. Procedure for High Precision Density Determinations by Hydrostatic Weighing. *J. Res. Natl. Bur. Stand. (U.S.)* **1967**, *71C*, 179.
- Burnett, B. S. Compressibility Determinations Without Volume Measurements. *J. Appl. Mech.* **1936**, *A136*, 58.
- Doulin, D. R.; Harrison, R. H.; Moore, R. T. Pressure-Volume-Temperature Relations of Hexafluorobenzene. *J. Chem. Thermodyn.* **1969**, *1*, 305.
- Duscek, W.; Kleinrahm, R.; Wagner, W. Measurement and correlation of the (pressure, density, temperature) relation of carbon dioxide. I. *J. Chem. Thermodyn.* **1990**, *22*, 827–840.
- Duscek, W.; Kleinrahm, R.; Wagner, W. Measurement and correlation of the (pressure, density, temperature) relation of carbon dioxide.

- II. *J. Chem. Thermodyn.* **1990**, *22*, 841–864.
- Ely, J. F.; Kobayashi, R. Isochoric Pressure–Volume–Temperature Measurements for Compressed Liquid Propane. *J. Chem. Eng. Data* **1978**, *23*, 221.
- Duarte-Garza, H.; Brugge, H. B.; Hwang, C.-A.; Eubank, P. T.; Holste, J. C.; Hall, K. R. Thermodynamic Properties of CO₂ + N₂ Mixtures. GPA/GRI Research Report RR-140, 1995.
- Goldman, K.; Scrase, N. G. Densities of Saturated Liquid Oxygen and Nitrogen. *Physica* **1969**, *44*, 555.
- Goodwin, R. D. Apparatus for Determination of Pressure-Density-Temperature Relations and Specific Heats of Hydrogen to 350 Atmospheres at Temperature above 14 K. *J. Res. Natl. Bur. Stand. (U.S.)* **1961**, *65C* (4), R224.
- Grigor, A. F.; Steele, W. A. Density Balance for Low Temperatures and Elevated Pressures. *Rev. Sci. Instrum.* **1966**, *37*, 51.
- Hales, J. L. An Apparatus for Accurate Measurement of Liquid Densities over an Extended Temperature Range. *J. Phys. E* **1970**, *3*, 855.
- Haynes, W. M. Simplified Magnetic Suspension Densimeter for Absolute Density Measurement. *Rev. Sci. Instrum.* **1976**, *48* (1), 39.
- Haynes, W. M. Measurement of Densities and Dielectric Constants of Liquid Propane from 90 to 300 K at Pressures to 35 MPa. *J. Chem. Thermodyn.* **1983**, *15*, 419.
- Hwang, C.-A.; Duarte-Garza, H.; Eubank, P. T.; Holste, J. C.; Hall, K. R. Thermodynamic Properties of CO₂ + CH₄ Mixtures. GPA/GRI Research Report RR-138, 1995.
- Kell, G. S. Density, Thermal Expansivity, and Compressibility of Liquid Water from 0° to 150 °C: Correlations and Tables for Atmospheric Pressure and Saturated Reviewed and Expressed on 1968 Temperature Scale. *J. Chem. Eng. Data* **1975**, *20* (1), 97.
- Kleinrahm, R.; Wagner, W. Measurement and correlation of the equilibrium liquid and vapour densities and the vapour pressure along the coexistence curve of methane. *J. Chem. Thermodyn.* **1986**, *18*, 739.
- Kratky, O.; Leopold, H.; Stabinger, H. Determination of the Partial Specific Volume of Proteins by the Mechanical Oscillator Technique. *Methods Enzymol.* **1973**, *27*, 98.
- Kratzke, H.; Muller, S. Thermodynamic Quantities for Propane. 3. The Thermodynamic Behavior of Saturated and Compressed Liquid Propane. *J. Chem. Thermodynamics* **1984**, *16*, 1157.
- Lau, W. R. A Continuously Weighed Pycnometer Providing Densities for Carbon Dioxide + Ethane Mixtures Between 240 and 350 K at Pressures up to 35 MPa. Ph.D. Dissertation, Texas A&M University, College Station, TX, 1986.
- Leopold, H.; Jelinek, R.; Titz, G. P. The Application of the Mechanical Oscillator Technique for the Determination of the Density of Physiological Fluids. *Biomed. Tech.* **1977**, *22*, 231.
- Machado, J. R. S.; Streett, W. B. Equation of State and Thermodynamic Properties of Liquid Methanol from 298 to 489 K and Pressures to 1040 bar. *J. Chem. Eng. Data* **1983**, *28*, 218.
- Masui, R.; Davis, H. A.; Levelt-Sengers, J. M. H. A New Magnetic Suspension Densimeter for Determining Fluid Densities by Weighing. *Proc. 8th Symp. Thermophysical Properties, ASME* **1981**, *1*, 128.
- Reding, J. N. Densities and Molal Volumes of Molten Magnesium Chloride, Potassium Chloride, and Barium Chloride Mixtures. *J. Chem. Eng. Data* **1965**, *10* (1), 1.
- Shana'a, M. Y.; Canfield, F. B. Liquid Densities and Excess Volume of Light Hydrocarbon Mixtures at 0165 °C. *Trans. Faraday Soc.* **1968**, *64*, 2281.
- Setzmann, U.; Wagner, W. A fundamental equation and tables of thermodynamic properties for methane covering the range from the melting line to 623 K at pressures up to 1000 MPa. *J. Phys. Chem. Ref. Data* **1991**, *20*, 1061.
- Shraiber, L. S.; Kukolenko, O. V. Technique for Precision Measurement of Liquid Density over a Wide Temperature Range. *Russ. J. Phys. Chem.* **1965**, *39*, 281.
- Thomas, R. H. P.; Harrison, R. H. Pressure, Volume, Temperature Relations of Propane. *J. Chem. Eng. Data* **1982**, *27*, 1.
- Tomlinson, J. R. Liquid Densities of Ethane, Propane, and Ethane-Propane Mixtures. Technical Publication TP-1; Natural Gas Processors Assoc.: Tulsa, OK, 1971.
- Van Witzenburg, W.; Stryland, J. C. Density Measurements of Compressed Solid and Liquid Argon. *Can. J. Phys.* **1968**, *46*, 811.

Received for review January 7, 1997. Accepted April 11, 1997.[®] The authors gratefully acknowledge financial support during the period of this work from the National Science Foundation, the Gas Research Institute, the Gas Processors Association, and the Texas Engineering Experiment Station.

JE970008X

[®] Abstract published in *Advance ACS Abstracts*, June 1, 1997.