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Apparatus for Density and Dielectric Constant Measurements to 35 MPa on Fluids of Cryogenic Interest

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An apparatus has been developed for simultaneous measurements of fluid densities and dielectric constants at temperatures from 70 to 320 K and at pressures to 35 MPa. A magnetic suspension technique, based on an application of Archimedes' principle, is employed in the density determination, while a concentric cylinder capacitor is used for obtaining the dielectric constant data. The apparatus can be used not only for determining densities and dielectric constants of compressed gases and liquids (including mixtures), but for saturated liquid and vapor properties as well. Also included is the capability for acquiring liquid-vapor equilibrium data for mixtures. The total uncertainty of a single density measurement is estimated to be approximately 0.1% for densities as low as 50 kg/m^3; at lower densities, the uncertainty increases. The imprecision of the density data is typically less than 0.02%. The total uncertainty in the dielectric constants is approximately 0.01%. Experimental data for a 0.85 CH_4+0.15 C_2H_6 mixture are given here to demonstrate the performance of the apparatus.

Key words: Clausius-Mossotti function; compressed fluid; concentric cylinder capacitor; density; dielectric constant; excess volume; magnetic suspension densimeter; methane-ethane mixture; saturated liquid; vapor pressure.

1. Introduction

A magnetic suspension densimeter [1,2][1] was used in a large-scale program to measure the orthobaric liquid densities of the major components [1,3,4] of liquefied natural gas (LNG) and mixtures [5–9] of these components. This technique, based on an application of Archimedes' principle, was selected for the LNG density project for several reasons:

1) It is capable of absolute density measurements of high accuracy and precision over wide ranges of density, temperature, and pressure.
2) Calibration fluids are not required.
3) The technique can be used not only to measure densities of compressed fluids, but also to measure liquid and vapor densities along the coexistence boundary.

The measurements for the LNG density project were concentrated in the temperature range from 100–140 K at pressures typically less than 0.2 MPa. The apparatus was designed for a maximum pressure of 5 MPa. Near the end of the LNG density project, the pressure range of the densimeter was expanded to at least 35 MPa. The expansion was because of a need to map the PVT surfaces of fluids with critical points significantly above ambient temperature. (A gas expansion technique [10–13] used at this laboratory for PVT measurements on cryogenic fluids could not be used for this application.) The expansion of the densimeter's pressure capability resulted in a new instrument, described here, significantly different from and more versatile than the previous one [1] developed specifically for the LNG density project.

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[1] Figures in brackets indicate literature references at the end of this paper.

Although many of the components of the new densimeter changed, the technique used is the same. To detect the position of the magnetic buoy, a linear differential capacitance sensor [12], compatible with the higher pressure environment, has been developed to replace an inductance sensor. Although the properties of the buoy had been well characterized in the previous work [1], it was necessary to determine the effect of pressure on its volume. A new support coil for lifting the buoy and a new microscope lens combination for determining the position of the buoy were also required in adapting the technique to higher pressures.

Since the dielectric constant of a fluid is closely related to its density through the Clausius-Mossotti function, a concentric cylinder capacitor was added inside the sample cell to enable simultaneous measurements of dielectric constant and density on the same fluid samples. Dielectric constant measurements can serve as simple and reliable substitutes for density measurements. The addition of the capacitor was motivated to some extent by the fact that some commercial densimeters being developed for custody transfer applications in LNG transactions include devices based on capacitance measurements.

The new apparatus incorporates a cryostat design different from that employed with the previous densimeter, but similar to ones used with other instruments [10–13] in this laboratory. The cryostat is suitable for continuous temperature control between 70 and 320 K. A new high-pressure window design developed for the equilibrium cell allows the position of the buoy to be determined by optical means. With the new cell and cryostat, it was not possible to change the position of the buoy by mechanical means; this is now accomplished electronically.

The apparatus can also be used for liquid-vapor equilibrium measurements on mixtures. Means have been provided for mixing (recirculation of vapor through liquid), sampling of vapor and liquid, and subsequent composition analysis. Compared to the previous densimeter [1], improvements have been made in the characterization of the temperature, pressure, and composition of the fluid samples. With the previous apparatus [1], it was possible to observe the liquid-vapor interface through a window that extended most of the length of the sample space. In adapting the magnetic suspension densimeter for pressures to 35 MPa over a wide temperature range, it was not practical to retain this feature. This feature, although convenient, was not essential for any of the measurements performed with the new apparatus.

The new apparatus was first used to complete measurements for the LNG density project [7,9]. Extensive tests were made to ensure that the density results obtained with the new apparatus were in agreement with those from the previous apparatus. The consistency of the density data was one of the most important considerations in the development of mathematical models [15–18] for predictions of mixture (LNG) densities. The apparatus was then used to measure the densities and dielectric constants of liquid propane [19–20], isobutane [19,21], and normal butane [19,22] over temperature ranges from their triple points to 300 K at pressures to 35 MPa.

2. Measurement Methods

2.1 Density

In the magnetic suspension densimeter used, a piece of magnetic material (barium ferrite magnetic buoy in the shape of a right circular cylinder magnetized along its cylindrical axis) is suspended freely by the force produced from the axial magnetic field of a single air-core solenoid. The vertical motion of the magnetic buoy is controlled by the automatic regulation of the solenoid current with a closed-loop servocircuit that includes a differential capacitance sensor to detect the position of the buoy. (The horizontal position of the buoy is maintained by the axially symmetrical, diverging field of the solenoid.) In the present system, the magnetic buoy is more dense than the fluids in which it is suspended. Thus, an upward magnetic force is added to the buoyant force to balance the downward gravitational force.

In earlier work [2] with a densimeter that utilized a three-solenoid arrangement to supply the magnetic force, it was found that the magnetic moment of a barium ferrite buoy was independent of magnetic field intensity over the range of fields (0.006–0.016 T) needed to support the buoy. Barium ferrite is a magnetically hard material with a permanent moment. This meant that a one-coil system could be used to determine fluid densities without the need of calibration fluids. To carry out density measurements with a one-coil system and a barium ferrite buoy, first the current (I_v) necessary to support the buoy in vacuum at a given position (buoy-coil separation distance) and temperature is measured. Then the current (I_f) necessary to support the buoy in a fluid of unknown density at the same position and temperature is determined. The density (ρ) of the fluid is related to these currents by the relation,

$$\rho = \frac{m}{V}\left(1 - \frac{I_f}{I_v}\right), \quad (1)$$

where m and V are the mass and volume of the buoy. Measurement procedures for using this equation to determine fluid densities for the instrument developed in the present work are discussed later. Also presented is a detailed description of the magnetic suspension system.

2.2 Dielectric Constant

A stable concentric cylinder capacitor was used for dielectric constant measurements. First, the capacitance (C) with the fluid (of unknown dielectric constant) between the cylindrical electrodes is measured. Then, at the same temperature, the vacuum capacitance (C_o) is determined. The dielectric constant (ϵ) is calculated from the relation,

$$\epsilon = C/C_o. \tag{2}$$

3. Apparatus

3.1 Cryostat

The major features of the cryostat are shown to scale in figure 1, an assembly drawing of the apparatus. This cryostat is similar to some used previously at this laboratory [10–13]. Those modifications necessary to adapt the cryostat for use with a magnetic suspension densimeter will be emphasized.

The cryostat was supported by a 1.3-cm-thick aluminum plate suspended from concrete block columns at a height 2.3 m above floor level. The aluminum plate was reinforced with 10-cm-wide stainless steel channel beams so that the position of the cryostat was independent of the amount of liquid nitrogen in the reservoir. Apparent changes in the buoy-coil separation distance resulted if the position of the cryostat was not maintained during the course of measurements. The aluminum plate from which the cryostat was suspended could be leveled and clamped in place using four bolts in contact with the concrete block columns.

The cryostat was fabricated from nonmagnetic materials. The inner cylinders or cans (liquid nitrogen reservoir, cold ring, guard ring, shield, cold wall) were copper; the outer vacuum jacket and access tubes were primarily stainless steel; and the flanges, support plates, and fittings were mostly brass. The various cylindrical portions of the cryostat and the central support (reflux) tube had to be aligned (concentric and vertical) so the buoy could be suspended symmetrically about the cylindrical axis of the differential capacitance sensor. Many of the dimensions of the cryostat components were determined by the dimensions of the high-pressure cell and the support coil. The outside diameter of the stainless steel vacuum jacket is 20.3 cm while the outside diameter of the glass tail of the cryostat is 9.0 cm. There is 0.4-cm clearance on the diameter between the cryostat tail and the support coil. The

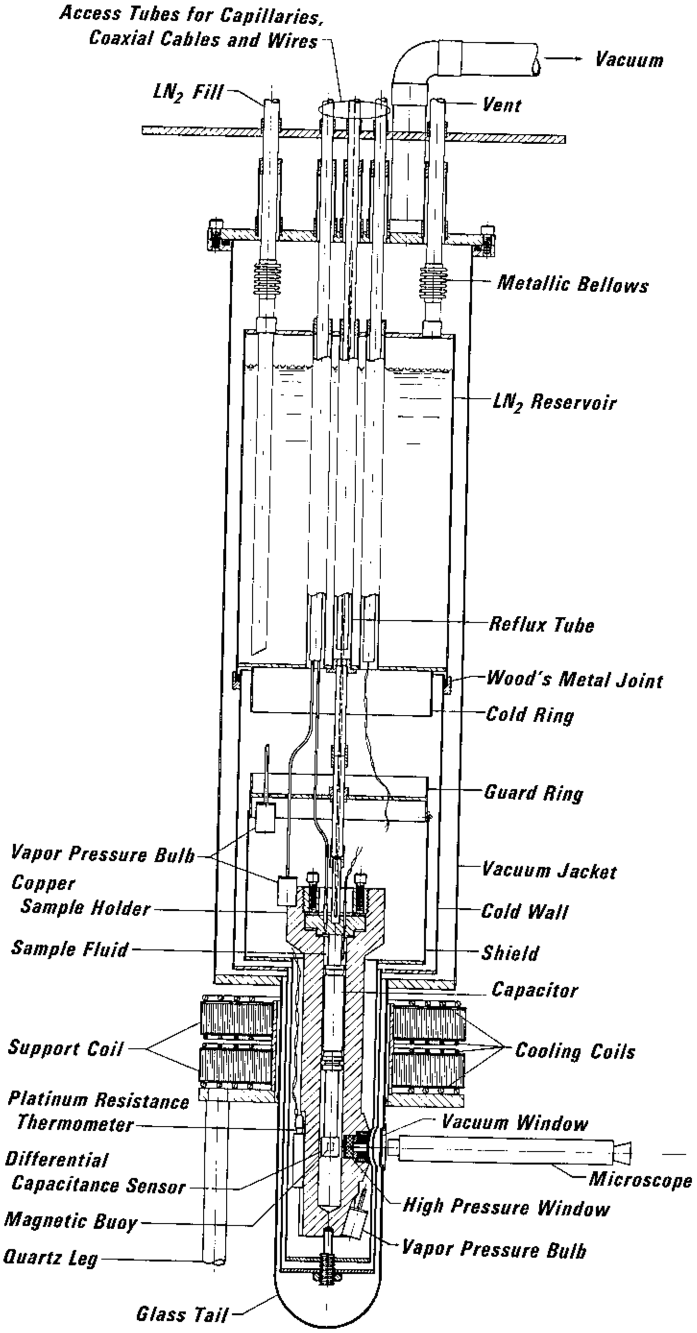

Figure 1–Assembly drawing (approximately to scale) of an apparatus for density and dielectric constant measurements to 35 MPa on cryogenic fluids.

overall length of the cryostat is approximately 94 cm.

The liquid nitrogen reservoir has a capacity of approximately 7×10^3 cm^3 and needs refilling under normal conditions about every 16 h. Metallic bellows were placed in the fill and vent lines of the reservoir to eliminate relative movement, as a function of temperature, between the cell and the outer stainless steel jacket of the cryostat. This step was necessary to maintain alignment of the capacitance sensor and buoy located inside the cell with the support coil located outside the cryostat, independent of the experimental conditions. Five access tubes, which passed through the liquid nitrogen reservoir, were available for introducing capillaries, coaxial cables, and wires into the vacuum space and cell inside the cryostat.

The cryostat was comprised of one large vacuum space; holes (3 cm diameter) were cut into the electroformed copper cylinders attached to the liquid nitrogen reservoir and the guard ring for visual observation of the buoy. With this arrangement it was not feasible to use exchange gas for fast-cooling the cell. The exchange gas would have been in direct contact with the outer stainless steel can which included a glass tail as its lower section. The glass tail was connected to the outer jacket through a stainless steel-to-glass transition joint; to ensure integrity of this seal, the joint should be kept at a temperature near ambient.

Fast-cooling of the cell was accomplished using the refluxing action of nitrogen in the central support tube. The maximum cooling rate was approximately 50 K/h. The reflux tube is evacuated during measurements when the cell is controlled at a desired temperature. For additional cooling, three flexible copper braided straps (not shown in fig. 1), each with a cross sectional area of 5 mm^2 per strap, have been connected symmetrically from the top of the cold shield to the cell.

The cryostat was designed to facilitate ease in assembly and disassembly and to minimize alignment problems of critical components. All demountable joints had enough latitude to make alignment reasonably straightforward. The outer vacuum jacket was attached to the top of the cryostat through a rubber o-ring seal using a split-ring assembly not shown in the drawing. The inner cans were attached with either Wood's metal or screws. Once the joints were secured, the entire structure was rigid, and no problems with alignment were encountered after numerous temperature cycles. A nut and bolt (fiberglass) arrangement was installed between the cold shield and the bottom of the cell to eliminate pendulous vibrations of the cell.

3.2 Equilibrium Sample Cell

Figure 2 is a detailed cross sectional diagram of the copper equilibrium cell. The overall dimensions of the cell used here are roughly the same as for the cell used with the earlier version [1] of the magnetic suspension densimeter, except for an increase in the wall thickness required for use at higher pressures. The new cell has an overall length of approximately 29.5 cm, primarily determined by the position at which the buoy must be suspended relative to the diverging field of the support coil for horizontal stability of the buoy. The outside diameter of the main part of the cell is 4.44 cm, while

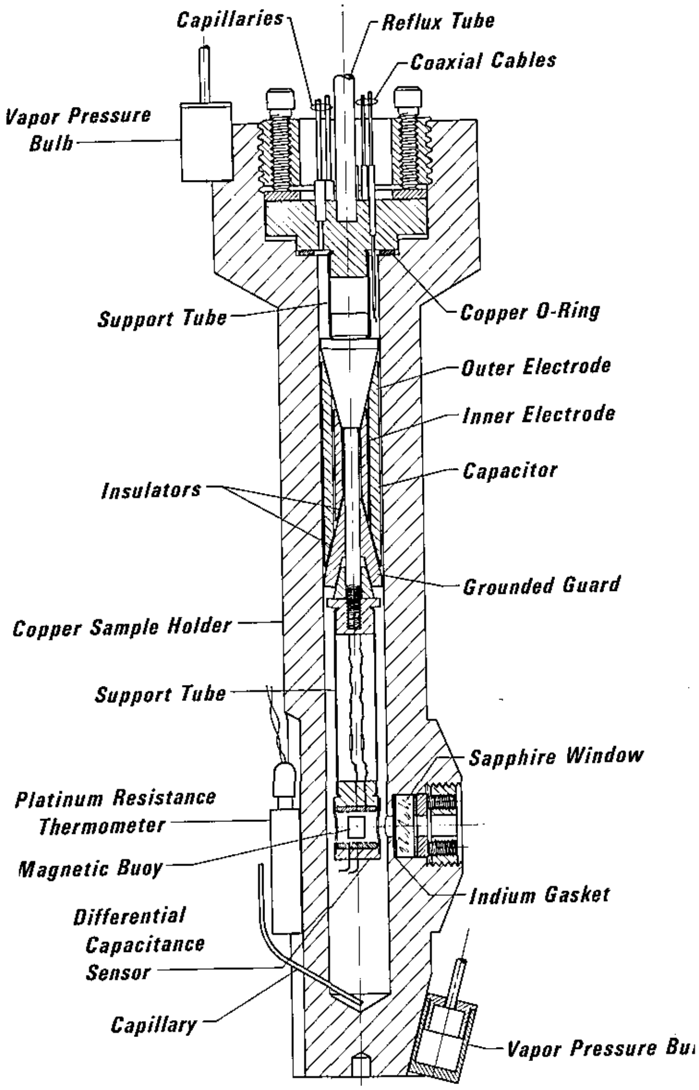

Figure 2–The equilibrium cell.

the top closure section has a diameter of 8.10 cm. The dimensions of the internal sample space are 1.90 cm diameter by approximately 23 cm length. About one third of the internal volume is occupied by the concentric cylinder capacitor and the magnetic buoy-capacitance sensor assembly. This results in an internal free volume of approximately 43 cm^3, as determined by filling the cell with water.

To facilitate easy access to the assemblies inside the cell, a flange-gasketed seal was used to close the cell. The seal was effected by compressing a silver-plated, solid copper O-ring between a stainless steel plug and a smooth, flat ledge of the copper cell. This assembly was similar to that used earlier [1]. A thin-walled stainless steel tube, used to support the cell, was soldered into the cell lid (the stainless steel closure plug). This support tube was also used for reflux gas as described earlier.

For visual observation of the magnetic buoy position, a new window assembly for pressures to 35 MPa has been developed. The assembly consists of a sapphire disk (1.90 cm diameter by 0.63 cm thickness) with chamfered edges, indium gasket, asbestos-rubber backing ring to relieve thermal and mechanical strains, and stainless steel plug and ring with four stainless steel set screws to provide a pressure- and vacuum-tight seal. It has a 0.63 cm diameter viewing area. An effort was made to minimize the size of the high pressure window assembly, especially in the horizontal direction. This effort resulted from an attempt to minimize the inner diameter of the support coil so current and power in the coil were not excessively large.

A total of four capillaries has been introduced into the sample space. Two capillaries are soldered into collars in the cell lid; the other two are soldered into the cell wall with their ends terminating at the bottom of the sample space. This makes it possible to fill the cell from either the top or bottom, or from both simultaneously. Filling procedures can be critical when condensing liquid mixtures into the cell. Under normal conditions, a pair of capillaries, one at the top and one at the bottom, is available for recirculating the vapor through the liquid for mixing; the other capillary at the top is for pressure measurements while the free capillary at the bottom can be used for liquid sampling. By having capillaries at both ends of the cell, it is easy to remove low vapor pressure liquids from the cell.

At approximately the same height at which the magnetic buoy is suspended, a platinum resistance thermometer has been soldered with indium into a closed-end copper tube that has been soft-soldered into a groove cut lengthwise in the cell wall. Vapor pressure bulbs fabricated from copper (each with an internal volume of approximately 2 cm^3) have been installed at the ends of the cell in close thermal contact (soft-solder) with the outside surface. These bulbs, along with differential thermocouples (chromel-constantan) secured at the same positions, are used to monitor temperature differences between the ends of the cell. Four independent heaters of 110 to 160 Ω each for temperature control have been wound bifilarly at different positions along the length of the cell.

A total of six coaxial cables enter through the lid of the cell into the sample space in pressure-tight assemblies. Three of the cables are for the capacitance sensor, two for the cylindrical capacitor, and one is a spare. Each coaxial cable consists of an outer stainless steel sheath of 0.51 mm diameter insulated from a 0.13 mm diameter inner conductor with polytetrafluoroethylene. These cables have been found to be leak-tight along short lengths at gas pressures to 70 MPa at room temperature. Cables approximately 1 meter in length have been inserted into stainless steel capillaries (1.07 mm outside diameter × 0.66 mm inside diameter) that extend from inside the sample cell to a position above the top of the cryostat where the coaxial cables are soldered into the capillaries. This means that continuous lengths of the coaxial cables extend from inside the sample cell to a region in which the cables are leak-tight. At low temperatures, the cables do not seal because of the relatively large difference in the thermal expansion coefficients of stainless steel and polytetrafluoroethylene. The stainless steel capillaries are soldered into collars in the lid of the cell and at the top of the cryostat.

3.3 Magnetic Suspension System

The magnetic suspension system, employed here in the density determination, uses some components from the previous densimeter [1]. The magnetic buoy, with its well-characterized properties deduced from the earlier work, has been described in detail. The buoy is a barium ferrite magnet in the shape of a right circular cylinder (0.51 cm diameter × 0.64 cm length) magnetized along its cylindrical axis. Barium ferrite is a magnetically hard, ceramic material with a density of approximately 5×10^3 kg/m^3. Since barium ferrite is porous, the buoy was plated with copper to a thickness of approximately 0.06 mm. A thin (10^{-3} mm) protective coating of gold was flashed over the copper. No problems were encountered with fluids penetrating the copper layer at pressures to 35 MPa.

Barium ferrite was selected as the buoy material since its magnetic properties are consistent with absolute density measurements [2]. Over the range of magnetic fields needed to support the buoy, the magnetic moment of the barium ferrite buoy had been found to be independent of the magnetic field intensity.

The densimeter described here included a single solenoid that supplied the force required to lift the buoy. The simplification in the densimeter design in going from a three-coil to a one-coil system, which resulted from a determination of the magnetic properties of barium ferrite, has been discussed in detail in an earlier paper [2]. (Although no further use of a three-coil arrangement with gradient coils was anticipated, the outside diameter of the new support coil was made less than the inside diameter of the gradient coils used in the previous work [1] in the eventuality that a need for tests on new buoy materials ensued.)

The new support coil is composed of two separate coils of 2275 turns each of epoxy-coated aluminum foil of approximately 0.025 mm thickness and 2.5 cm width. Each of the two coils, epoxied to a central quartz tube at a separation distance of 1.3 cm, has an inside diameter of 10.16 cm and an outside diameter of roughly 22.2 cm. To be compatible with the new higher-pressure cell, the inside diameter of the new coil is somewhat larger than that used previously [1]. The quartz tube is attached to a fiberglass plate supported by three quartz rods (2.54 cm diameter) that extend to another fiberglass plate resting on a part of the concrete block structure, used for rigid support of the entire apparatus. Water-cooled copper plates, insulated with thin mylar sheets, have been placed in close thermal contact with all faces of the two coils. No problems have been encountered with this arrangement for mounting and cooling the coils for use at currents to 1.5 A, which corresponds to 270 W heat dissipation in the coils.

The servocircuit is essentially the same as that used before [1] except for a new type of sensor for detecting the position of the buoy. Some problems had been encountered with the earlier densimeter [1] with pressurized fluid slowly penetrating into the coil windings of an inductance sensor, resulting in a slow change in the position of the suspended buoy. Thus, a differential capacitance sensor [13], a solid monolithic structure, has been developed for position detection in the present work that entails measurements in fluids at pressures to 35 MPa. The sensitivity of the capacitance sensor was at least equivalent to that of the linear differential transformer used previously. By balancing a bridge of which the sensor is a part, the position of the buoy can be made insensitive to the dielectric constant of the sample fluid. For a detailed description of the capacitance sensor, see reference [13].

The previous densimeter [1] included mechanical means for fine adjustment of the position of the buoy in going from vacuum-to-liquid measurements. The new system does not incorporate this feature. Small changes in the buoy position are accomplished electronically in the new system by adjusting the offset voltage of the integrator amplifier in the servocircuit. A calibrated 0.5-Ω standard resistor, placed in series with the support coil, can handle the relatively large currents needed to lift the buoy in the present work. The measurement of the voltage drop across this resistor, which is immersed in an oil bath, enters directly into the density determination.

A 125x filar micrometer microscope is used to determine the position of the buoy. A new lens combination, which includes an objective lens (38 mm) with a larger working distance (less power) and a higher-power (14x) eyepiece, gives approximately the same magnification as with the earlier apparatus [1]. The microscope is rigidly mounted on an aluminum support table, adjustable in three dimensions. The entire assembly is secured firmly with bolts to the massive concrete block structure.

3.4 Concentric Cylinder Capacitor

The capacitor for dielectric constant measurements was located in the top portion of the sample space, as seen in figure 2. The central support mandrel of the capacitor was connected rigidly to the sample cell lid using a slotted brass tube, crimped at its ends, that clamped tightly over mating surfaces on the mandrel and the lid. The same type of brass tube was used to connect the differential capacitance sensor to a nut at the bottom of the capacitor. The use of the brass tubes for support of the components inside the cell resulted in an extremely rigid assembly that provided means for independent rotational orientation of each component. The coaxial leads to the differential capacitance sensor located below the capacitor passed through the brass tubes and a slot in the central support mandrel of the capacitor.

The concentric cylinder capacitor design used in the present work was based on that developed by Younglove and Straty [23]. Two slightly different capacitors are used with the present apparatus, depending on whether the measurements are for mixtures or for pure fluids. For mixture measurements, slots are cut into the cylinders parallel to the cylindrical axes, similar to the ring and bar design of Pan et al. [24]. This modification was made to minimize the chances for composition gradients in the cell by allowing free passage of fluid mixtures between the electrodes. The vacuum capacitance of the capacitor with slotted cylinders was approximately 20 pF, while that for the one with solid cylinders was about 33 pF.

The dimensions of the capacitors used here were proportionally the same as those of Younglove and Straty [23]; however, the overall size was significantly smaller. The overall external dimensions of each capacitor were 6.4 cm length × 1.77 cm diameter. For the capacitor with slots, the widths of the five slots in each cylinder were 0.32 cm, while the slot lengths in the outer cylinder were 4.1 cm and those in the inner cylinder were 1.9 cm. The outside diameter of the inner cylinder was 1.06 cm. The outer cylinder had a thickness of 0.32 cm, while that of the inner cylinder was 0.24 cm. There was a separation distance of 0.38 mm between the cylindrical electrodes. Small pieces of Kapton[2] film (0.05 mm thickness) were used to insulate the electrodes from the support assembly. Both of the capacitors were fabricated from copper. A thin protective coating of gold was flashed over the surfaces.

4. Measurements

4.1 Temperature and Pressure

The primary temperature sensor, calibrated on the IPTS-68, is a platinum resistance thermometer, which had been used with the previous densimeter [1]. The uncertainty of the calibration is approximately 0.002 K. The potentiometric system for temperature measurements gives uncertainties that range from approximately 0.010 K at 100 K to 0.030 K at 300 K. The temperature of the sample space is regulated within a few mK, approximately the same as the reproducibility of the temperature measurements. A current of 1 mA for the thermometer, supplied by an electronic constant current source, is determined to an uncertainty of approximately 0.002%. The total uncertainty in the measured temperatures is estimated to be less than 0.03 K.

Vapor pressure measurements on liquid nitrogen, methane, ethane, and propane at temperatures from 100–290 K have been used to check the calibration of the thermometer. Temperatures from vapor pressure measurements, using selected data from the literature, generally agreed with measured temperatures (platinum resistance thermometer) to better than 0.02 K. Further details on temperature measurements are presented in reference [1].

Temperature differences between the ends of the cell are monitored with vapor pressure bulbs located at the ends of the cell. The bulbs have been filled with the fluids mentioned above, the selected fluid depending on the temperature range needed. With the reflux tube evacuated, overall temperature differences were typically less than 0.01 K, or within the precision of the vapor pressure measurements. Thus, a differential thermocouple, with junctions placed near the vapor pressure bulbs, was not needed as part of a control loop to regulate the temperature distribution along the length of the cell.

A third vapor pressure bulb was soldered in close thermal contact with the guard ring. This vapor pressure bulb was used to check a differential thermocouple between the guard ring and the cell. This thermocouple was part of a control circuit to maintain the temperature of the guard ring approximately equal to that of the sample cell. The guard ring was connected to a copper radiation shield that surrounded the cell to provide an approximately isothermal environment for the sample space.

The techniques and instrumentation for control of the temperature of the cell are standard. Four independent heaters along the length of the cell are available, if needed, to minimize temperature gradients. Only the middle two heaters have been used in the control circuit. It should also be noted that temperature gradients along the length of the cell can be monitored by observing the vapor pressure of the liquid inside the cell as a function of the liquid level.

Pressures of the fluid under test are usually measured with a dual-range, precision oil dead-weight gauge. Its sensitivity ranges from 2×10^{-4} MPa at 3 MPa to 2×10^{-3} MPa at 35 MPa. The overall uncertainty in pressure is approximately 0.01%, increasing somewhat at lower pressure. With the high range piston, this gauge cannot be used for pressures less than 0.2 MPa; with the low range piston, the lowest pressure is approximately 0.04 MPa.

A spiral quartz Bourdon-tube gauge with a range of 0–1.38 MPa is normally used for vapor pressure measurements. It has been calibrated against an air dead-weight gauge; maximum uncertainty in the

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[2] In order to describe materials and experimental procedures adequately, it is occasionally necessary to identify commercial products by manufacturers' or trade names. In no instance does such identification imply endorsement by the National Bureau of Standards, nor does it imply that the particular product is necessarily the best available for that purpose.

calibration was 70 Pa. The resolution of this gauge is better than 20 Pa.

Both pressure gauges are characterized by relatively small free volumes, approximately 0.5 cm^3 for each. This is an important consideration when performing mixture (phase equilibria) measurements with this apparatus, e.g., to minimize vapor space corrections.

4.2 Density

The accuracy and precision of density measurements with the magnetic suspension technique used here depend on a knowledge of the mass and volume of the buoy, along with the capability to determine the position of the buoy with high resolution independent of the medium in which the buoy is suspended. The same barium ferrite buoy as used with the previous densimeter was employed here; its properties have been well characterized and are discussed elsewhere [1]. The mass of the buoy is 0.73706 g and its volume at 300 K is 0.13485 cm^3. Thermal expansion data [25] for barium ferrite were previously obtained to calculate the volume of the buoy at low temperatures. The change in the volume of the buoy for a temperature change from 100–300 K is approximately 0.4%.

The earlier densimeter was used at relatively low pressures compared to those used now. Based on the properties of similar materials, it was estimated that the effect of pressure on the volume of the barium ferrite buoy was negligible ($<0.001\%$) for the highest pressures (2.5 MPa) encountered with the previous densimeter. Since the new apparatus is used at pressures up to 35 MPa, bulk modulus measurements [26] have been carried out on a sample of barium ferrite, the buoy material. Bulk modulus (B_T) data (in units of MPa) from 75–295 K are represented as a function of temperature (T in units of K) by the expression,

$$B_T = B_{295}\left(1.01629 - \frac{0.0206014}{e^{\frac{175.15}{T-75}} - 1}\right), \tag{3}$$

where $B_{295} = 1.3030 \times 10^5$ MPa, the bulk modulus at 295 K. Coefficients were determined from nonlinear least squares. The correction to the volume of the buoy at room temperature for a pressure of 35 MPa amounts to 0.027%.

For density measurements, it is necessary to suspend the buoy at the same position relative to the support coil in vacuum and in the test fluid at the same temperature. Although the microscope lens combination (sec. 3.3) used here is different from that of the previous densimeter, the present arrangement results in position measurements of the same quality. The maximum error in the position determination is 2×10^{-3} mm, which corresponds to an error in density of less than 0.03% for a density of 5×10^2 $\mathrm{kg/m^3}$, or larger.

The position of the buoy is observed through a 0.63 cm thick sapphire window in the cell. It has been observed that the apparent position of the buoy changes slowly with the pressure inside the cell; as the cell volume expands, the angle of the sapphire window changes. The magnitude of this effect has been determined as follows. First, the microscope is adjusted so that the position of the buoy is independent of the index of refraction of the fluid inside the cell. This procedure is accomplished by observing the buoy resting at a stationary position on the capacitance sensor assembly as the cell is alternately filled with gas and liquid at a pressure slightly greater than 0.1 MPa; e.g., methane at 120 K. The temperature of the cell is maintained during these tests. Then, the cell is filled with liquid at a pressure less than 0.1 MPa; either propane, isobutane, or normal butane have proved ideal for these tests at temperatures between 100 and 300 K. Then, the pressure inside the cell is increased to greater than 35 MPa while observing the buoy at rest on the sensor assembly. The change in the index of refraction for a 35-MPa change in pressure along an isotherm for liquid propane, isobutane, or normal butane is negligible compared to the change in refractive index in going from vapor-to-liquid for methane at 120 K. The change in position with pressure corresponds to a change in density with pressure of less than 5×10^{-2} $\mathrm{kg/(m^3 \cdot MPa)}$ for liquid methane at 120 K.

The currents in the support coil needed to suspend the buoy in vacuum and in the fluid of interest (see eq (1)) are determined by measuring the voltage drops across a 0.5-Ω standard resistor in series with the support coil. The voltages were routinely measured to 5×10^{-6} V with a high resolution differential-type voltmeter, which corresponds to a change in density of less than 0.01% for a density of 5×10^2 $\mathrm{kg/m^3}$.

4.3 Dielectric Constant

The dielectric constant is determined from a measurement of the ratio of the capacitance of the concentric cylinder capacitor with fluid between the electrodes to the capacitance under vacuum. The capacitances are measured with a three-terminal ac bridge operated at an oscillator frequency of 5 kHz. Measurements to a resolution of 10^{-6} can be obtained with little difficulty with this bridge.

Both capacitors used in this work yielded equal results within the precision of the measurements in tests on liquid methane. Measurements on mixtures are inherently more difficult and are generally characterized by greater scatter because of the difficulties associated with obtaining homogeneous liquid mixtures in the sample space. Examples of dielectric constant measurements on pure fluids and mixtures with the apparatus described here are given in references [7,19–22,27].

Measurements of the vacuum capacitance are normally obtained just before or just after fluid measurements are performed. Since vacuum measurements are required for each run in the density measuring technique used here, there was no reason vacuum capacitances should not be recorded at the same time. Thus, there was no reason to acquire a calibration curve representing the vacuum capacitance as a function of temperature. Vacuum measurements can be made to a precision of 10^{-4} pF and are usually stable within 0.0002 pF when the sample cell is cycled between low temperature and room temperature. (Vacuum capacitances have been observed to be stable to better than 10^{-3} pF for more than 20 temperature cycles over a period of several months.) The total change in the vacuum capacitance from 300–100 K is approximately 0.3%. Based on tests by Younglove and Straty [23] on a similar cylindrical capacitor, the effect of pressure on the capacitor was sufficiently small to neglect. It is estimated that, based on the resolution of the capacitance measurements and the stability of the capacitor design, the total uncertainty in the dielectric constant measurements is approximately 0.01%.

5. Performance of Apparatus

5.1 Results and Discussion

Before completing measurements for the LNG density project, it was necessary to ensure that the new densimeter yielded results consistent with those from the previous densimeter. First, density data were obtained for several components of LNG (e.g., methane, ethane, etc.); the data obtained with the new apparatus agreed to better than 0.02% with the results [1,3,4] determined at the onset of the LNG density project with the earlier version [1] of the magnetic suspension densimeter. As mentioned earlier, measurements on saturated liquid methane were used as a check on the measurement process during the entirety of the LNG density project. Dielectric constant data for liquid methane exhibited differences of <0.01% when compared with the data of Straty and Goodwin [28].

Next, data were obtained for a binary mixture of methane and ethane, a system that had been extensively investigated with the earlier densimeter. The data for three mixtures of methane and ethane had been used to optimize several mathematical models [15–18] developed for prediction of LNG densities. The most accurate and versatile of these models was the extended corresponding states method [15–17]. The new data for a methane+ethane mixture would be compared with predictions from this model. The mixture, for which data are reported here, had also been used to cross-check results from this laboratory obtained with the magnetic suspension densimeter with those from another laboratory that employed an entirely different technique for determining density [29]. The experimental density of Miller and Hiza [29] for this methane+ethane mixture at 110.08 K differed by 0.01% from that calculated from the extended corresponding states model [16].

The experimental orthobaric liquid densities, vapor pressures, and dielectric constants of a 0.85147 CH_4+ 0.14853 C_2H_6 mixture are presented as a function of temperature in table 1. Excess volumes and values for the Clausius-Mossotti (CM) function, as well as values for the excess function, are also given in table 1. The excess volume (V^E) is defined by the relation,

$$V^E = V - \sum_i x_i V_i [1+\beta_i (p_i - p)], \tag{4}$$

where V is the molar volume of the mixture at a given temperature at saturation pressure p, V_i is the molar volume of component i at the same temperature at saturation pressure p_i, x_i is the mole fraction of component i, and β_i is the isothermal compressibility of component i. The CM function is defined by the expression,

$$\mathrm{CM} = \frac{1}{\rho}\left(\frac{\epsilon-1}{\epsilon+2}\right), \tag{5}$$

where ρ is the density and ϵ is the dielectric constant. Then the excess Clausius-Mossotti function (CM^E) for a liquid mixture is defined, analogous to V^E, by the relation,

$$\mathrm{CM}^E = \mathrm{CM} - \sum_i x_i \mathrm{CM}_i , \tag{6}$$

Table 1. Orthobaric liquid densities (ρ) and dielectric constants (ϵ) of 0.85147 CH_4+0.14853 C_2H_6 mixture (molecular weight = 18.1265 g·mol^{-1}) as a function of temperature (T) and pressure (P). ρ_{CSM}, density calculated from extended corresponding states model; V^E, excess volume; CM, Clausius-Mossotti function; CM^E, excess Clausius-Mossotti function.

$\frac{T}{K}$	$\frac{P}{MPa}$	$\frac{\rho}{mol \cdot dm^{-3}}$	$\frac{10^2(\rho_{expt}-\rho_{CSM})}{\rho_{CSM}}$	$\frac{V^E}{cm^3 \cdot mol^{-1}}$	ϵ	$\frac{CM}{cm^3 \cdot mol^{-1}}$	$\frac{CM^E}{cm^3 \cdot mol^{-1}}$
115.00	0.116	25.3618	−0.059	−0.410	1.67297	7.2243	0.005
120.00	0.166	24.9911	−0.013	−0.493	1.66070	7.2220	0.000
125.00	0.232	24.5983	−0.045	−0.567	1.64828	7.2239	−0.001
130.00	0.316	24.1950	−0.036	−0.655	1.63561	7.2258	−0.003

where CM refers to the Clausius-Mossotti function of the mixture at a given temperature at the saturation pressure of the mixture, and CM$_i$ is the Clausius-Mossotti function of pure component i at the same temperature and pressure as the mixture. Adjustments of the pure component CM$_i$'s to the saturation pressure of the mixture are sufficiently small to neglect.

In the calculation of V^E and CM$_i$, the pure component molar volumes of methane and ethane were calculated from equations in references [1,3] obtained from fitting experimental orthobaric liquid densities determined with the earlier version of the magnetic suspension densimeter used in the LNG density project. Vapor pressures for methane and ethane were taken from Goodwin [30] and from Goodwin et al. [31], respectively. Isothermal compressibilities for methane were taken from Rowlinson [32]; those for ethane from Miller [33]. The dielectric constants of Straty and Goodwin [28] were used for methane, while those of Weber [34] were used for ethane.

Also presented in table 1 are comparisons between the experimental densities (ρ_{expt}) from this work and densities (ρ_{CSM}) calculated from the extended corresponding states model [15–17]. The average absolute deviation is 0.038%. This result, combined with the pure fluid comparisons, demonstrates that data obtained with the new densimeter are consistent with data taken with the previous instrument. The total uncertainty of a single density measurement for these binary mixture data is estimated to be ±0.1%. The present results are also consistent within experimental error with the data point of Miller and Hiza [29] for the same mixture.

The calculated excess Clausius-Mossotti values were less than 0.07% of the mixture CM values for the methane+ethane mixture data presented here. This result was expected based on dielectric constant and density measurements on other mixtures containing nonpolar constituents [7,9,24]. It appears that the excess CM values show a slow decrease with increasing temperature.

After the new apparatus had been thoroughly tested, it was used to complete the measurements for the LNG density project [7,9]. Next, the apparatus was used to obtain data for propane [19–20], isobutane [19,21], and normal butane [19,22] at pressures up to 35 MPa. The performance of the apparatus at high pressures is demonstrated by these pure fluid data.

5.2 Error Analysis

Detailed discussions of the systematic and random errors involved in measurements with the magnetic suspension densimeter used in the present work have been presented elsewhere [1,3–9, 19–22]. The uncertainty in the density measurements depends primarily on the uncertainties in the determination of the volume of the buoy, of the relative position of the buoy and the support coil, and of the temperature of the sample fluid. With the new apparatus, designed for higher pressures than the previous one, the effect of pressure on the apparent position of the buoy, resulting from slight movement of the cell window, must now be included. Maximum uncertainty in the density determination resulting from this effect is 0.02%.

The effect of pressure on the volume of the buoy, which is extremely small at maximum design pressure of the cell, must also be considered. As discussed in section 3.3, the reduction in the buoy volume for a pressure of 35 MPa is 0.027%. The uncertainty involved in this adjustment is negligible.

As discussed [1], the total uncertainty of a single density measurement is taken as the square root of the sum of the squares of the systematic errors plus an allowance of three times the standard deviation for random error. The imprecision of measurement (or standard deviation) is typically less than 0.02%. Both the precision and accuracy of density measurements with a magnetic suspension densimeter depend on the difference between the density of the buoy and the density of the fluid. For the present arrangement, where the density of the buoy is significantly larger (typically an order of magnitude) than the density of the fluids, the precision and total uncertainty change slowly with fluid density. The total systematic error in the measurement process from known sources is approximately 0.05% at low temperatures, decreasing to approximately 0.03% at room temperature. This results in an estimated total uncertainty in the density of approximately 0.1% at low temperatures and 0.06% at room temperature. (Of course, the uncertainty in the density determination also depends on the values of the derivatives, $(\partial\rho/\partial P)_T$ and $(\partial\rho/\partial T)_P$, for the particular region of the PVT surface for the fluid under investigation.)

The uncertainties in the dielectric constant determination have been discussed in detail (sec. 4.3 and refs. [7,9,19–22]). The total uncertainty in the dielectric constant measurement is estimated to be approximately 0.01%.

The estimates of the uncertainties in the density and dielectric constant measurements can be tested to some degree by making comparisons with reliable data from independent sources. Such comparisons have been made for many fluids over wide ranges of experimental parameters (such as temperature, pressure, density, etc.) [7,9,19–22]. In general, these comparisons have confirmed the estimates of the uncertainty levels.

There has been little information presented in this paper concerning the problems associated with mixture measurements compared to pure fluid measurements. The uncertainties involved in the determination of the composition of mixtures have been discussed in detail in previous papers [1,5–9].

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