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Review on Natural Gas Thermopysical Property Measurement Techniques

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1. Introduction

Since it is impossible to measure the thermodynamics properties of all systems in nature, we must rely upon mathematical models to extrapolate the available experimental data. In order to develop such models, very accurate experimental data are necessary for selected complex mixtures, such as those that exist in natural gas. For this reason researchers must collect the most important and fundamental thermodynamics properties for such systems. Two of the most important thermodynamics properties are the pressure volume (density) and temperature ($P\rho T$) surface and the phase equilibrium properties of mixtures. Accurate volumetric property data are used in custody transfer operations for natural gas. Also accurate $P\rho T$ data are necessary for calculating energy functions. On the other hand, phase equilibria data are needed mostly for design calculations involving separation processes. Additionally, very accurate phase equilibrium knowledge is necessary for natural gas transfer through pipelines to avoid condensation in the pipelines. Atilhan et. al. [1] have shown that even widely used equations of state (EOS) such as Peng-Robinson or Redlich-Kwong (RK) cannot predict the retrograde condensation region for simple natural gas-like mixtures that do not contain heavy fractions.

When natural gas rises from the reservoir to the ocean floor at offshore platforms, the stream temperature can drop quickly (perhaps 5 to 10 °C) until it reaches the surrounding ocean temperature. This rapid temperature drop at high pressure along with moisture in the natural gas stream make conditions favorable for gas hydrate formation in the pipeline. Hydrates can cause several serious problems such as: plugging the pipeline and blowouts [2]. Similar problems are as well common in natural gas compression facilities at offshore and onshore processing plants. Such problems can be avoided by increasing the temperature and insulating the stream that comes from the ocean bed, or by lowering the pressure of the pipeline. Another possible solution is lowering the dew point of water in the

stream by adding polar solvents to the line such as methanol or glycols. In order to apply all these methods, accurate knowledge on PρT behavior of the natural gas stream is necessary.

Because of their importance, density measurements essential for both industrial applications and scientific research. Very accurate PρT data is required not only to calculate custody transfer of natural gas in pipelines but also to develop new EOS for industrial and scientific use. Experimental PρT data is employed to calculate thermal properties of fluids required for industrial process design calculations. Loss of accuracy from density predictions directly impacts processes; therefore only exceptionally good density values ensure good thermal properties [3].

Knowledge of temperature, pressure and composition enables determination of the density from an EOS. The equation most widely used in custody transfer of natural gas is the Detailed Characterization Method or AGA8-DC92 EOS developed by American Gas Association (AGA) in 1992 [4]. This EOS was derived using an extensive and reliable experimental PρT database that included real natural gas mixtures as well as high order hydrocarbon mixtures (mostly binary mixtures of natural gas components). AGA8-DC92 EOS has different accuracy regions as shown in Figure 1.
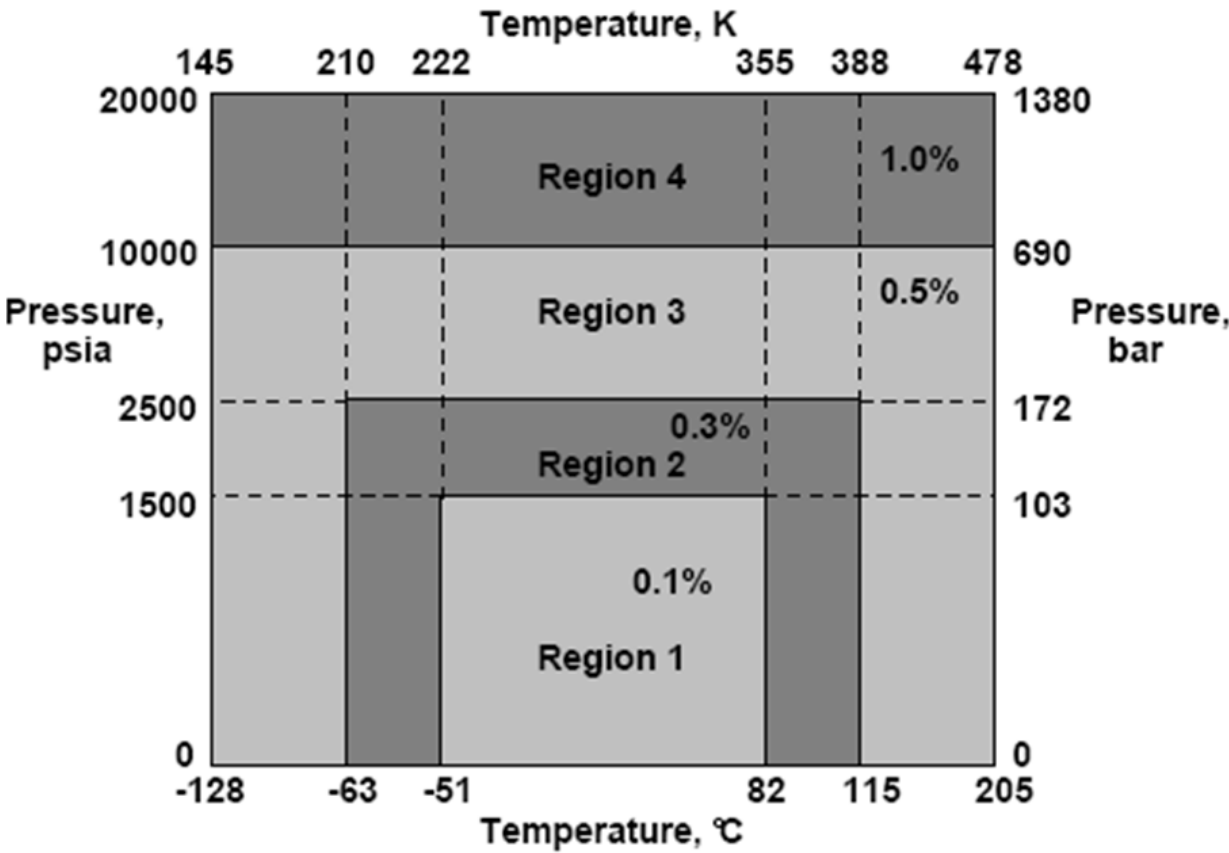
Figure 1. AGA8-DC92 EOS uncertainty regions [**5**].

As seen in Figure 1, the maximum uncertainty claimed for the EOS is 0.1% in region 1, 0.3% in region 2, 0.5% in region 3 and 1.0% in region 4. However, the equation is valid only for

lean natural gas mixtures over this wide range of conditions, and its ability to describe rich natural gases is untested. The equation cannot perform equilibrium calculations, as it is only valid for gas phase calculations. Also, use of the equation is not recommended near the critical point. The deviations from density measurements are 2 to 2.5% for North Sea natural gas samples at 8 to 17 MPa and 40 to 80 °C [6]. Following this, the Gas Research Institute (GRI) and National Engineering Laboratory (NEL) started a collaborative, joint industry project to extend the range of applicability of AGA8-DC92 EOS for natural gas mixtures to include the gas compositions observed in the North Sea. GERG-2008 EOS is the latest benchmark EOS that addresses the drawbacks of AGA8-DC92 EOS and it has proven to have better uncertainty in PρT predictions [7].

2. Density measurement techniques

2.1. Introduction

This section contains reviews of several experimental methods for density measurements, and discusses the relative strengths and weakness of each method. An EOS can describe the thermodynamic state or vapor liquid equilibrium (VLE) of pure fluids and mixtures with accuracy that depends upon the application. The accuracy of an EOS depends upon the experimental data used during development of the equation. Historically, the quality of predictions obtained from EOS has improved dramatically as advanced technologies and new instrumentation have become more common for experimental methods. Among the thermodynamic properties, density is the most directly predicted property using EOS. The measured densities should be approximated by suitable EOS and the measurements should be traceable to the International System of Units [8]. According to Kleinrahm et. al. [9], the following considerations are important when deciding upon a density measurement technique:

i.   Large pressure and temperature range for wide operations.
ii.   Low total uncertainty and high accuracy of the method for the overall range.
iii. Simplicity in design and ease of maintenance and operation.
iv.   Little time required for each data point measurement.

2.2. Density measuring devices

Several different density-measurement techniques are described in this section, including: speed of sound methods, vibrating body techniques, continuous weighing method and buoyancy-based densimeters.

2.2.1. Speed of sound methods

Speed of sound measurements can be used to determine the performance of an equation of state for thermodynamics property predictions. By correlating the speed of sound to thermodynamics properties, one can build experimental devices and investigate solid,

liquid and gas thermodynamics properties for pure components and mixtures. Densities and isothermal and isentropic compressibility factors result from speed of sound measurements experiments [10]. Based upon a pulse technique described by Daridon et. al. [11], a cylindrical-shaped cell is used to measure ultrasonic waves. In the pulse technique, effects of pressure upon piezo-electric materials are isolated by separating piezo-electric elements from the fluid studied. The speed results from the measurements of the transit time through the sample and the length of passage, which is a function of temperature and pressure. Density comes from:

$$\rho(P,T) = \rho_0(P_0,T_0) + \int_{P_0}^{P} u^{-2}dP + \int_{P_0}^{P} \left(\alpha^2 / C_p\right)dP \tag{1}$$

In above equation u is the sound speed, α is the isobaric coefficient of thermal expansion, C_p is the isobaric heat capacity and P_o is the atmospheric pressure. The sum of these terms gives the density with as a function of pressure at different temperatures. The first integral, where can be expressed as a polynomial in pressure with coefficients expressed as polynomials in temperature, can be evaluated along the isotherms considered. By using thermodynamics relations for α and C_p, the second integral can be calculated iteratively. The second integral is a few percent of the first integral. More detailed discussion on numerical evaluations for such measurements appears in [10] and [11].

2.2.2. Vibrating devices

Vibrating tubes and vibrating forks are common density measuring techniques. These devices measure the fluid density of interest by determining the oscillation frequency of the vibrating element in the fluid. These instruments provide accurate results quickly. However, frequent calibration is necessary for this apparatus to maintain its accuracy [12]. Moreover, when the density of the fluid is vastly different from air or pure water (frequently used as reference fluids because of their well-known thermophysical properties) the uncertainty of the measurements increases as reported by Kuramoto et al. [8].

2.2.2.1. Vibrating wires

In vibrating wire densimeters, a wire carrying a diamagnetic weight is suspended in the fluid to be monitored. The wire is placed in a robust position in a uniform magnetic field provided by permanent magnet in both vertical and horizontal directions. When an alternating current passes through the power source to the wire, interaction starts with the current and the magnetic field. This leads to induced harmonic motion that is orthogonal to the magnetic field and the wire. If the mass, density and the dimension of all the solid components of the system are known, the resonant frequency of the wire can be determined experimentally under vacuum conditions. If the viscosity of the fluid of interest is known, experimental measurement of resonant frequency of wire velocity provides the fluid density [13; 14]. Although the vibrating wire technique is suitable for a wide range of pure fluid and mixture gas density applications, it suffers from problems such as surface tension on the wire, adsorption on the weight, detailed knowledge need of exact dimensions of the wire

and the assembly. However, the device is used widely as a primary densimeter device because it has a simple operating principle and allows development of an exact physical model. Density, in principle, can be calculated directly from the theory.

2.2.2.2. Vibrating tubes

Vibrating tube densimeters consist of an assembly that includes two thin walled metallic or glass tubes bent in Y or V shapes as shown in figure 2. A permanent magnet and drive coil reside between these two tubes. Generally, a drive coil and a permanent magnet are placed in the middle of the two tubes. The drive coils and magnet are mounted on the opposite legs of the tubes. Each coil and magnet on the side leg forms a pick-off circuit. Alternatively, attractive and repulsive magnetic fields between the coils and magnets are provided by sending alternating current to the drive coil.
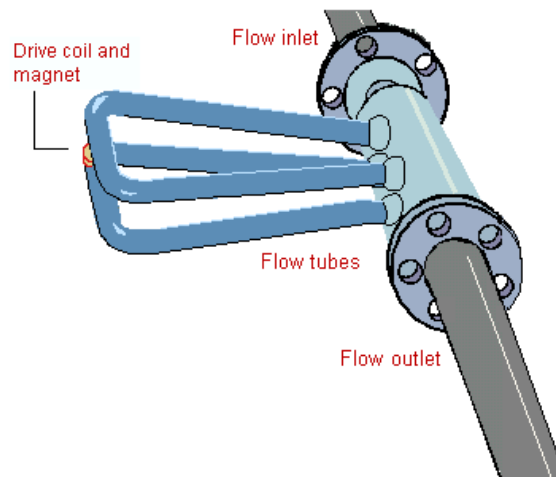
Figure 2. Vibrating tube densimeter scheme.

Because the drive coils and the magnets are installed on the opposing side of the tubes, a sine wave generated by the two pick-up circuits represents the motion of one tube relative to the other. The sine waves are in phase if there is no flow in the tube. The density of the fluid is:

$$\rho = K\tau^2 + L \tag{2}$$

where, tube parameters K and L are both pressure and temperature dependent and τ is the period of vibration. Because it is not possible to determine the temperature and pressure dependence of K and L, measurements are performed at the same temperature and pressure conditions with the sample. A reference fluid of well-known properties is used for this reason. Finally, the corresponding density difference equation is:

$$\rho - \rho_r = K\left(\tau^2 - \tau_r^2\right) \tag{3}$$

where subscript r stands for the reference fluid. ρ and τ are not exactly linear, and this must be taken into consideration. The vibrating tube densimeters are designed for rapid operation

and they perform very precise measurements of density differences. If one assumes linearity between ρ and τ, the highest levels of accuracy expectations are not achieved.

2.2.3. Expansion devices: Burnett method

Another well-established and widely-used density measurement device is the Burnett apparatus. Burnett [15] suggested a technique to measure the densities of sample fluids without measuring the mass or volume directly. An expansion device contains two cells. During operation, the sample is charged initially into the first cell and, after pressure and temperature measurement, expanded into the second cell. The ratio of the final volume to the original volume equals the ratio of densities before and after the expansion. Only pressure and temperature are measured before and after expansion of the sample from a single volume (V_A) into the combination of the original volume and a second volume ($V_A + V_B$). Some of the gas goes through a sequence of isothermal expansions into a chamber, which is evacuated every time the expansion takes place. Both virial coefficient and gas density can be calculated with this method. The ratio of the densities before and after the expansion is calculated for each expansion:

$$\rho_i = \rho_m \pi_\infty^{m-i} \prod_{j=i+1}^{m} \left[\frac{1 + \gamma_{ab} P_j}{1 + \gamma_a P_{j-1}} \right] \tag{4}$$

where

$$\pi_\infty = \lim_{P \to 0} \frac{V_a + V_b}{V_a} \tag{5}$$

In equation 4, γ_a and γ_{ab} are the pressure distortions of the volumes V_a and ($V_a + V_b$) respectively, π_∞ is the zero pressure cell constant, ρ_m is the density at the lowest pressure and subscripts i and superscript m indicate the value after the i-th and m-th (last) expansions, respectively. A serious problem that can affect the Burnett apparatus is adsorption of the sample gas on the inner surfaces of the measuring cell [16]. Also a Burnett apparatus is difficult to automate fully because of frequent valve operations. Because of error accumulation, very high precision is necessary in the pressure measurements, which necessitates use of high-quality dead-weight gauges. The adsorption affect can be minimized by the using two cells with a surface area ratio almost equal to the volume ratio [17]. Eubank et al. have formulated new adsorption correction schemes, based upon the BET adsorption isotherm [18].

2.2.4. Continuously weighed pycnometer method

In the continuously weighed pycnometer method, the mass of the sample is determined by direct weighing of the cell. A typical pycnometer consists of a weight measurement system, constant temperature bath, temperature control system and data acquisition system, a

volume bellows cell for changing pressure and density without transferring mass, and a high vacuum system [19]. The major component of this method is a constant volume pycnometer suspended from a digital balance. The pycnometer can be filled and evacuated with an extension tube that enables faster measurements and reduces operator errors. The mass of the pycnometer when empty and when filled with fluid is measured by a digital balance. The density of the fluid being measured at constant temperature and pressure is calculated from the measured mass value of the fluid and the known volume of the pycnometer. One disadvantage of this method is that the long feed tube exposes part of the sample to ambient temperature making it impossible to measure mixture densities when the sample exists as one phase at the cell set point temperature and at room temperature.

2.2.5. Hydrostatic buoyancy methods

The hydrostatic buoyancy force technique is based upon Archimedes' Principle. Basically, Archimedes' Principle states "when a solid body is immersed in a fluid, it displaces a volume of fluid the weight of which is equal to the buoyancy force exerted by the fluid on the sinker." This means that the buoyancy force is proportional to the density of the fluid in the measuring cell under pressure. This principle can be applied to determine the gas density of any pure fluid or mixture. Historically, improvements have appeared in the application of buoyancy method based densimeters.

2.2.5.1. Classical methods

In classical hydrostatic buoyancy densimeters, an object (sinker hereafter), usually a sphere or cylinder, is suspended from a commercial digital balance by a thin wire. The fluid is kept in a pressure cell at constant temperature using a temperature control mechanism. The sinker is submerged in the fluid and weight of the sinker is constantly monitored. According to Archimedes' principal, the apparent loss in the true weight of the sinker is equal to the weight of the displaced fluid. Density of the fluid results from:

$$\rho = \frac{m_V - m_a}{V_S(T,P)} \tag{6}$$

In above equation m_v is the 'true' mass of the sinker in vacuum, m_a is 'apparent' mass of the sinker in the fluid and V_s is the calibrated volume of the sinker, which is a function of temperature and pressure. In such densimeters, several corrections are necessary to reduce the effect of surface tension between the sample liquid and the immersed part of the wire, and the effect of the buoyant force of air on the masses of the analytical balance. Zero shift of balance readings, buoyancy forces on auxiliary devices, adsorption effects and surface tension may reduce the accuracy of such measurements [20].

2.2.5.2. Magnetic suspension devices

To overcome limitations in achievable accuracy, the need for frequent calibration of the apparatus with reference fluids, complexity of operation, limitations on temperature and

pressure, Kleinrahm and Wagner [9] introduced an MSD based upon magnetic levitation of the sinker in the measuring cell. The novelty of the magnetic suspension coupling was that it used non-physical-contact force transmission between the sinker in the pressurized cell and the weighing balance at atmospheric pressure, thus allowing a cell design that covered a very wide temperature and pressure range [21]. Then, Kleinrahm and Wagner [20] modified the hydrostatic buoyancy force method by introducing an alternative force transmission method in which they levitated two sinkers through a magnetic suspension coupling. By compensation for surface tension, buoyancy, adsorption effects and shifts in zero-point of the balance, a two-sinker MSD improved the accuracy of the density measurements.

Operation of a two-sinker MSD is rather complex and its advantage is not required for medium or high-density measurements encountered in many practical applications. To extend the instrument range towards higher temperatures and pressures, Wagner et al. [16] have developed a single-sinker densimeter. Although the single sinker design is much simpler than that of the two-sinker densimeter, it is still possible to perform high-accuracy density measurements at relatively low gas densities by applying some of the advantageous features of the two sinker device [22]. The single-sinker densimeter also operates based upon Archimedes' principle and the force transmission comes from levitation of the sinker in the measuring housing of the high-pressure cell. Klimeck *et al.* [23] have concluded that the accuracy of density measurement from a single-sinker densimeter is lower than that from a two-sinker densimeter especially at low densities because it lacks compensation for the adsorption effect. Moreover, the force transmission error has more effect on total density measurement uncertainty than observed in a two-sinker densimeter. Also for small densities, having the load compensation system outside of the measuring cell is less effective than having it inside as with the two-sinker densimeter.

3. Viscosity measurement techniques

3.1. Introduction

Viscosity is a remarkable property for natural gas because of its influence on flow behavior, which is especially important for reservoir conditions. Natural gas viscosity is several orders of magnitude lower than for oil or water, and thus, natural gas mobility in reservoirs is larger than for water or oil. Moreover, gas flow is predominantly laminar in reservoirs, and thus, the influence of viscosity is especially important. The upstream gas industry faces new challenges for precision monitoring of gas supplies, for which accurate and reliable knowledge of the natural gas viscosity is a prerequisite. Davani et al. [24] and Denney [25] analyzed the gas viscosity estimation errors on the gas recovery from a high pressure-high temperature (HPHT) reservoir, showing that a -10 % error in gas viscosity estimation can produce a relative 8.22 % error in estimated cumulative gas production, and a + 10 % error can lead to a relative 5.5 % error in cumulative production. Moreover, uncertainty in gas viscosity data has a direct effect for inflow performance relationship curves [26], Davani et al. [27] showed that a 1 % uncertainty in gas viscosity data leads to a 1 % uncertainty in gas flow rate.

Sanjari et al. [28] reported in recent study that common prediction methods for natural gas viscosity lead to large deviations when applied for high pressure – high temperature ranges, and thus, these methods should be applied with caution for reservoir estimations. This lack of accuracy for current predictive viscosity models, and the large economical impact of viscosity uncertainties, show the need of experimental accurate natural gas viscosity to analyze *i*) the effect of natural gas composition on viscosity for wide pressure – temperature ranges, and *ii*) the predictive performance of current viscosity analyze the predictive performance of current viscosity predictive models and developing more accurate predictive approaches.

Experimental accurate measurement of gas viscosity is very difficult, requires properly designed equipment, especially for high pressure–high temperature conditions, and is very costly both in time and resources. Moreover, possible natural gas mixtures under experimental study is very large considering that natural gas composition depends strongly on the origin, age, and depth of the reservoir [29]. Likewise, conditions of interest, especially the high pressure – high temperature conditions found in many new reservoirs that can be explored with current technologies [30], has a remarkable effect on natural gas viscosity, and discard the use of traditional measurement techniques. The analysis of published viscosity data in the open literature shows its scarcity both in the number of studied systems and the experimental conditions (high pressure data are almost absent) [28,31]. Therefore, systematic studies on natural gas viscosity has to be carried out in wide pressure-temperature ranges and as a function of mixture compositions, for selected mixtures representative of key reservoirs. Our group is involved in a multilaboratory international research project in which natural gas viscosity is measured, and other relevant thermophysical properties, using state-of-the-art equipments [31,32]. As a result of our research, we report in this section a detailed analysis of the available experimental methods for measurement of natural gas viscosity.

## 3.2. Viscosity measuring devices

3.2.1. Rolling ball viscometers

Rolling ball viscometers measuring principle is based on the travelling time of a metal or glass ball through a known distance to measure the viscosity of the fluid, Figure 3. The ball of known diameter rolls down a tube of known length, at a known inclination, filled with the fluid under study, under isothermal-isobaric conditions.

The viscosity of the fluid is proportional to the ball travelling time, considering that the fluid flow around the ball is laminar. Sage and Lacey [33] proposed corrections to be applied in case of viscosity measurements under turbulent flow.

The working principle of rolling ball viscometers may be summarized in equation (7):

$$\eta(P,T) = k_1(P,T,\theta) \times t(\theta) \times (\rho_b - \rho) + k_2(P,T,\theta) \qquad (7)$$
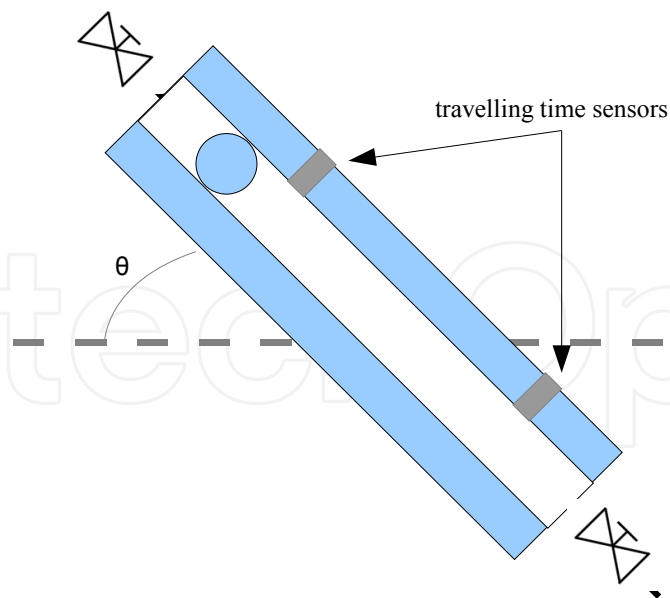
Figure 3. Scheme of a rolling ball viscometer.

Where ρ_b and ρ stand for the ball and fluid density, respectively, t for the ball travelling time, and k_1 and k_2 for the calibration constants, which are function of the measurement angle (θ). Calibration constants are obtained with fluids of known viscosity for the required pressure-temperature ranges. It should be remarked that rolling ball equipments are kinematic viscometers, and thus, and additional instrument is required for density measuring in the studied pressure-temperature ranges.

The use of rolling ball viscometers for gas measurements is very scarce, and high pressure data are almost absent. Sage and Lacey [33] measured viscosity data for methane and two hydrocarbon gases up to 2900 psi, Bicher and Katz [34] measured the viscosities of methane-propane mixtures up to 5000 psi. The uncertainty of viscosity measurements using rolling ball viscometers it is claimed to be ± 2 % when applied for measurements in the liquid state [35], although no detailed uncertainty analysis is available for gas measurements. Dolan et al [36] carried out gas phase measurements for n-butane using a capillary viscometer and showed large difference with rolling ball viscometer data by Sage et al. [37], who claimed a ± 5 % for their gas phase viscosity measurements.

3.2.2. Capillary tube viscometers

The working principle of classical capillary viscometers (so-called Rankine viscometers) is based on the introductions of a pellet of mercury into a tube filled with the gas under study, with the mercury pellet completely filling the cross section of the tube. The mercury pellet will reach a steady descending velocity will for any inclination of the tube. The descending pellet will act as a moving piston, which will force the gas through an adjacent capillary, leading to a constant pressure difference across the fine capillary. Gas viscosity is obtained from the measurement of the mercury pellet falling time between two fixed points. Capillary viscometers have been widely studied for gas measurement

because of their operational simplicity and the small amounts of required gas. Heath [38] analyzed the performance of capillary viscometers for gas phase measurements, and Kobayashi [39] carried out a detailed analysis of the application of Hagen-Poiseuille's law for gases to the Rankine viscometer. Giddings et al. [40] developed a high-pressure capillary viscometer, which was applied for measurements of methane, propane and their mixtures up to 544.4 atm with a 0.25 % claimed reproducibility. Lee et al. [41] carried out systematic measurements of the viscosity of natural gas mixtures using a capillary viscometer with an estimated accuracy of ±2.00. In a recent work, May et al. [42] obtained reference viscosity data for several gases, including methane, using a modification of capillary viscometer.

3.2.3. Vibrating wire viscometers

The falling body and the capillary tube methods for viscosity measurements require hydrodynamic corrections and approximations for ends, edges, and walls. These applied corrections are not always known, and in most cases are sources of important errors. These corrections are avoided by the use of vibrating wire based viscometers. These apparatus are based on the damping of the vibrations of a wire in the fluid under study. An applied external field disrupts the wire immersed in the fluid, leading to periodic oscillations. In the free-decay mode the damping of the oscillations depends on the viscosity and density of the fluid [43]. This technique can be applied in a straightforward manner to low viscosity fluids, in fact most of the available contemporary natural gas viscosity data have been measured using vibrating-wire based approaches. Tough et al. [44] and Trappeniers [45] were the first to apply vibrating wire devices for the measurement of low viscous fluids and gases at high pressures. Assael et al. [46] carried out viscosity measurements of a natural gas mixture with a claimed uncertainty of ± 1 % up to 15 MPa. Langelandsvik et al. [47] measured viscosity of three natural gas mixtures with a ± 1% estimated uncertainty up to 5.0 MPa. Schley al. [48] measured viscosity of methane and two natural gases up to 29 MPa with a ±0.3 % and ±0.5 % estimated uncertainties for methane and gas mixtures, respectively. Likewise, vibrating-wire viscometers are considered as quasi-primary measurement methods [43].

3.2.4. Falling body viscometers

The experimental setup for these instruments is very similar to that for rolling body viscometer with the exception that the ball is replaced with a piston. These equipments have been widely for measuring liquid viscosity but measurements for low viscous gases are scarce. In most cases the viscometer arrangement is vertical, which is a serious limitation for gas measurements considering the very short travelling times. Heidaryan et al. [49] used a falling body viscometer for measuring methane viscosity up to 140 MPa.

A modification of traditional falling body viscometers has recently proposed to withdraw the aforementioned disadvantages and to apply this equipment to large pressure

temperature ranges. In this equipment a piston is placed inside a cylindrical measuring chamber filled with the fluid (gas or liquid) under study, the piston is driven electromagnetically by two coils located at opposite ends and the time taken by the piston to complete one motion is correlated to the viscosity of the fluid in the measuring chamber by a working equation. A scheme of the equipment installed in our laboratory is showed in Figure 4. The measurement chamber is placed at 45º inclination, and the setup allows measurements from 0.02 to 10000 cp, simply changing the used piston.
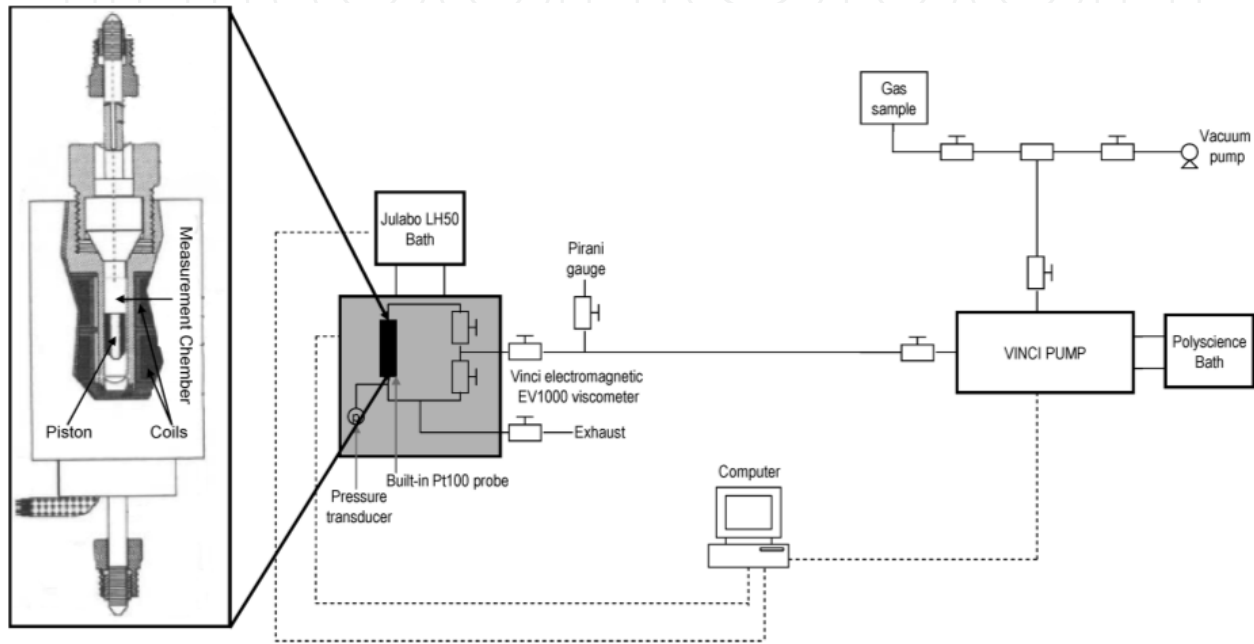

Figure 4. Electromagnetic viscosity measuring device [31].

The main advantage of this equipment is the ability to carry out fast measurements in wide pressure-temperature ranges. Nevertheless, Thomas et al. [50] and Viswanathan [51] reported problems for gas viscosity measurements using electromagnetic viscometers, mainly raising from the poorly defined pressure-temperature dependence of the measurement chamber properties. Therefore, we proposed a new calibration method using this equipment to avoid these problems, which was validated against reference viscosity data, leading ± 0.1 % reproducibility and to ± 2.5 % and ± 4.0 % uncertainties, for pressures lower than 30 MPa and higher than 30 MPa, respectively. Nevertheless, we should remark that the uncertainty values are derived from the uncertainties obtained from the calibration fluids. This is a remarkable problem for viscosity measurements, the use of secondary methods requires the knowledge of highly accurate viscosity data for reference fluids, in wide pressure – temperature ranges, which is not currently available [43]. Nevertheless, the use of electromagnetic based viscometer allow to obtain wide collection of viscosity data for gas mixtures, in wide pressure – temperature ranges, with acceptable accuracy and at moderate costs.

4. Phase equilibria measurement techniques

4.1. Introduction

The prediction of natural gas vapor–liquid equilibria is of primary importance for industrial purposes [52]. This property, together with the knowledge of PVT behavior, is required in all the stages of natural gas production / transportation chain. The vapor–liquid equilibria of natural gas mixtures is commonly analyzed using the pressure–temperature projection, so–called phase envelope, Figure 5, in which a curve separating the two–phase (vapor–liquid equilibria) and single–phase (vapor or liquid) regions is plotted.
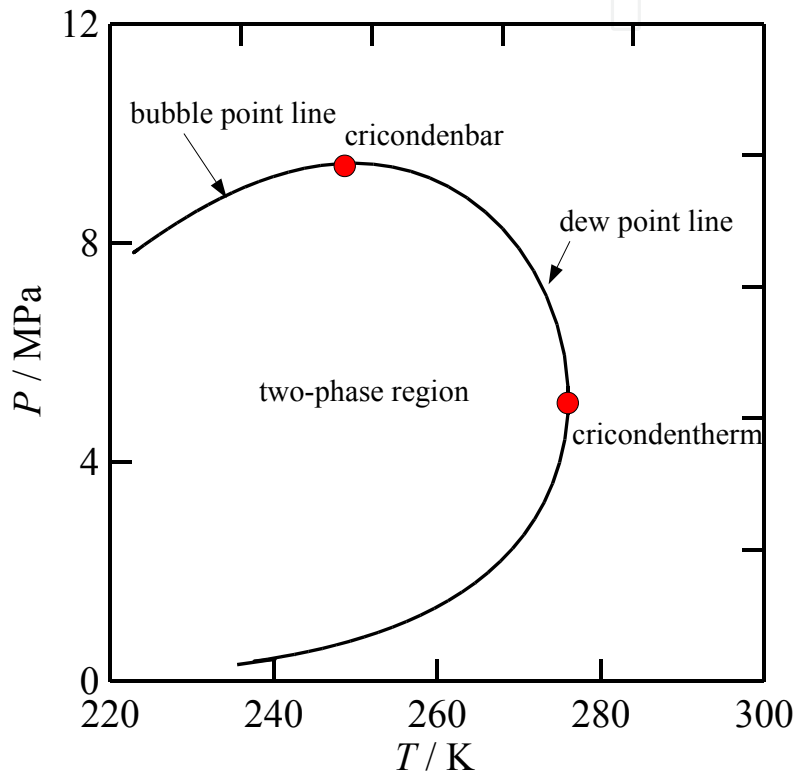
Figure 5. Phase envelope of a typical natural gas.

In this curve, three points are of remarkable importance: *i*) the critical point, where bubble and dew points curves meet, *ii*) the cricondenbar, the maximum pressure at which vapor and liquid phases may coexist, and *iii*) the cricondentherm, the highest dew point temperature. Therefore the importance of an accurate knowledge of natural gas phase envelopes could be summarized in three main areas: *i*) reservoir engineering, *ii*) custody transfer and *iii*) gas transportation through pipelines [53].

For reservoir engineering purposes, care must be taken to maintain the gas in single phase conditions because during exploration a pressure depletion may lead to an erroneous determination of reservoir composition (and thus to incorrect field–development designs), because dew point curve is crossed and liquid is formed, and during production liquid drop-out may lead to valuable hydrocarbons left behind in the reservoir [54]. If liquid drop-

out appears in the wellbore, it may lead to liquid loading concerns. For custody transfer purposes, the inaccuracy in the knowledge of phase envelopes may lead to contractual disputes rising from the contract sales gas dew point specifications between the company that sales the gas and the purchaser. For transportation through pipelines [29], it is essential to maintain the fluid pressure above the cricondenbar to protect the compressors which may be damaged by the presence of liquid drops [55]. Moreover, the sizing of the compressors depends on the value of the predicted cricondenbar, and thus, inaccuracy in the knowledge of this value may lead to an oversizing of the expensive compressors (if the real value is lower than the predicted ones) or to a two–phase flow (if the real value is above the predicted one) along the pipelines. Hence, accurate knowledge of phase envelopes allows reducing the design margins, to optimize the pipelines capacity, and thus, to improve the economic viability of new pipelines projects [56].

Therefore phase envelopes must be known before production / transportation operations are designed for any new gas–field. The most accurate and reliable way to obtain the phase envelope for any natural gas mixtures is its determination through experimental measurements [12] Nevertheless, these measurements require state–of–the–art apparatus, which are very costly, both in time and resources, and, considering that the composition, and thus properties, of natural gases can vary widely depending upon the reservoir from which the fluid comes, it is almost impossible carry out measurements for all the possible mixtures over the wide temperature and pressure ranges required. Thus, the common way to obtain phase envelopes for design purposes in the gas industry is through available theoretical models, using gas chromatography determined compositions, and thus, the reliability of the designs stands on the accuracy of the used models. In the natural gas industry, equations of state (EOS) are the common choice for phase equilibria predictions, and cubic EOS are mainly used because of their simplicity. Multiparametric EOS developed in the last years, such as AGA8–DC92 [4], which are used with high accuracy for density predictions are not applicable for phase equilibrium calculations or for liquid properties, and thus other EOS such as cubic ones or new multiparametric GERG2008 [7] are used to characterize natural gas. Nonetheless, the predictive ability of available models for phase equilibria have to be studied against accurate experimental data to test their reliability, and thus, experimental measurements for selected natural gas mixtures using accurate methods are required [57].

Experimental methods for measurement of vapor-liquid equilibria in high pressure conditions may be classified as *i*) analytical and *ii*) synthetic [58].

4.2. Phase equilibria measuring methods

4.2.1. Analytic methods

For the analytic method, pressure and temperature are fixed and then phase separation is produced, sampling for each phase under equilibrium is carried out and then composition is

determined by chromatographic methods. This technique may carried out using static or dynamic circulation approaches. The experimental results from this type of experimental equipment are usually isothermal or isobaric phase diagrams. Natural gas mixtures usually contain small fractions of heavy components (C_{6+} fractions), which are difficult to measure accurately through chromatographic methods, and thus, this approach is not very useful for the study of natural gas mixtures.

4.2.2. Synthetic methods

In the synthetic method a mixture of known composition is prepared and its behavior observed as a function of pressure or temperature. The experimental results from this type of equipment are isopleth phase diagrams. The synthetic method may be subdivided into visual and non-visual.

4.2.2.1. Visual synthetic methods

Chilled mirror dew point meters is the simplest and most widely applied method of hydrocarbon dew point measurement in the gas industry. These instruments have a metallic mirror surface inside a high-pressure sample cell. The instruments are also equipped with a glass viewing port through which operator can observe the mirror surface. Mirror dew point meters normally are used for periodic spot check measurements [59].

The principle of the mirror dew point meter is to observe the very first signs of condensate, Figure 6. Therefore, cooling samples for several pressures allows to build the phase envelope, Figure 7.
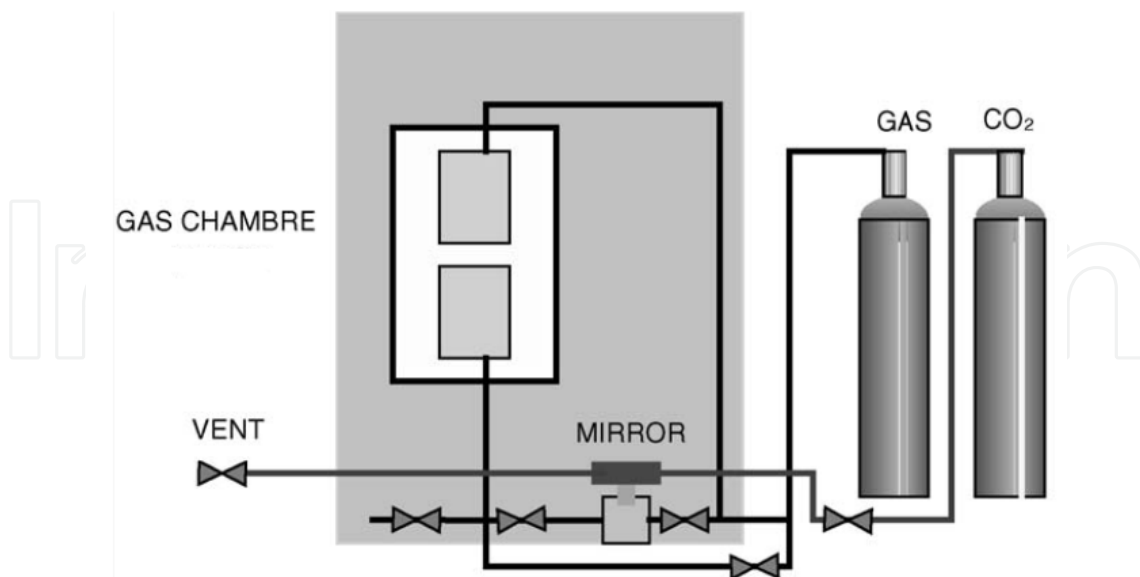
Figure 6. Scheme of a chilled mirror equipment for phase envelope measurements.

The main difficulties in making such a measurement lie in the characteristics of hydrocarbon condensates. The natural gas condensates are colorless and have low

surface tension. This means that the liquid film that forms as the sample cools through the dew point temperature is almost invisible to operators. At the same time, the decreasing temperature measurement reading must be observed as the mirror temperature drops. To achieve the best sensitivity and repeatability of measurement, the rate of mirror cooling is critical and should be as slow as possible through the region in which the dew point is likely to be found [60]. The subjective nature of such a measurement technique can result in large uncertainty in natural gas dew point measurement [59].
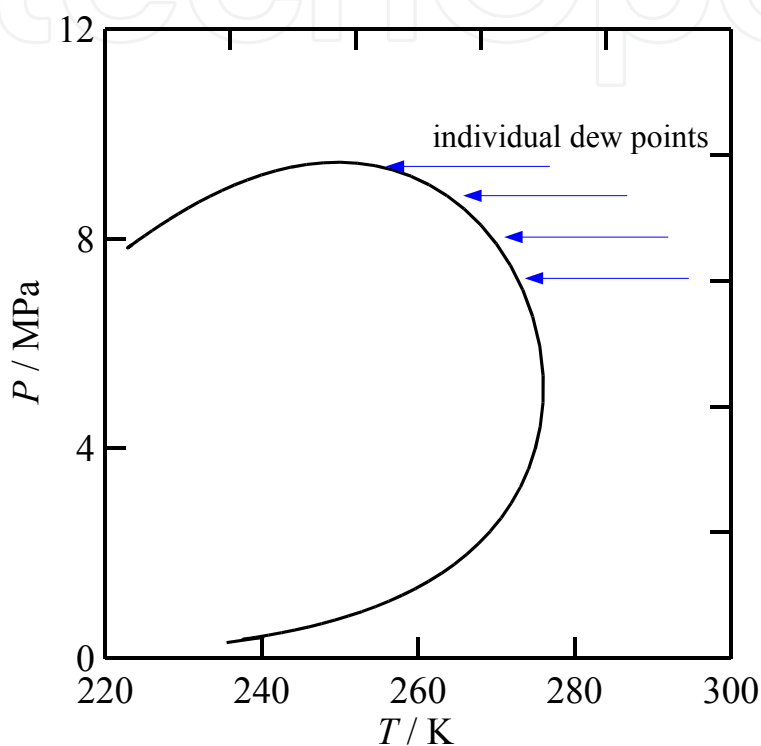

Figure 7. Scheme of experimental procedure for measuring phase envelopes using visual chilled mirror method.

4.2.2.2. Non-visual synthetic methods

The method usually involves a blind *pVT* cell filled in the single-phase region with a mixture of known composition. Variation of one of the measured quantities allows measurement of a second quantity while the third is held constant. Therefore, measurements are made along either an isobaric or isochoric or isothermal path with the homogenous / heterogeneous boundary (phase envelope) determined from a discontinuity in the slope of the other two variables [61]. Among the non-visual methods, the isochoric technique is probably the most useful for the determination of phase envelopes in natural gas mixtures, its amenability to automation allow the collection of large quantities of accurate data at moderate costs.

The technique for determining phase loops using isochoric method utilizes the change of the slope of an isochore as it crosses the phase boundary, Figure 8.

It should be remarked that the change of slope does not occur at the cricondentherm, which has a collinear isochore [62]. The apparatus cell volume changes slightly with pressure and temperature, and thus, experimental data require an application of the cell distortion equation to correct the results to truly isochores. In a recent work Acosta et al. [63] developed a new computational method for the analysis of isochoric data to obtain phase envelope experimental data points, reporting that the phase boundary temperatures and pressures could be determined within 0.45% and 0.04%, respectively. Our research group has developed a systematic measurement program on selected natural gas-like mixtures using the isochoric method with the cell design reported in Figure 9 [64-66]. The reported results allowed to analyze the predictive ability of the equations of state commonly used in the gas industry for phase envelope predictions showing large deviations, which justify the need of very accurate experimental data for the analysis and prediction of natural gas phase equilibria.
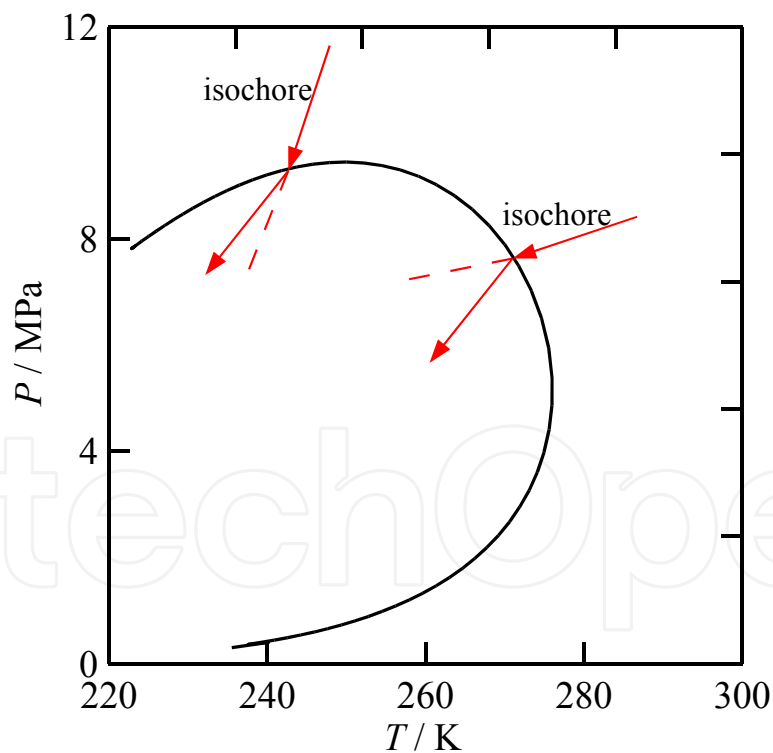
Figure 8. Method for determine phase envelope from isochoric measurements.
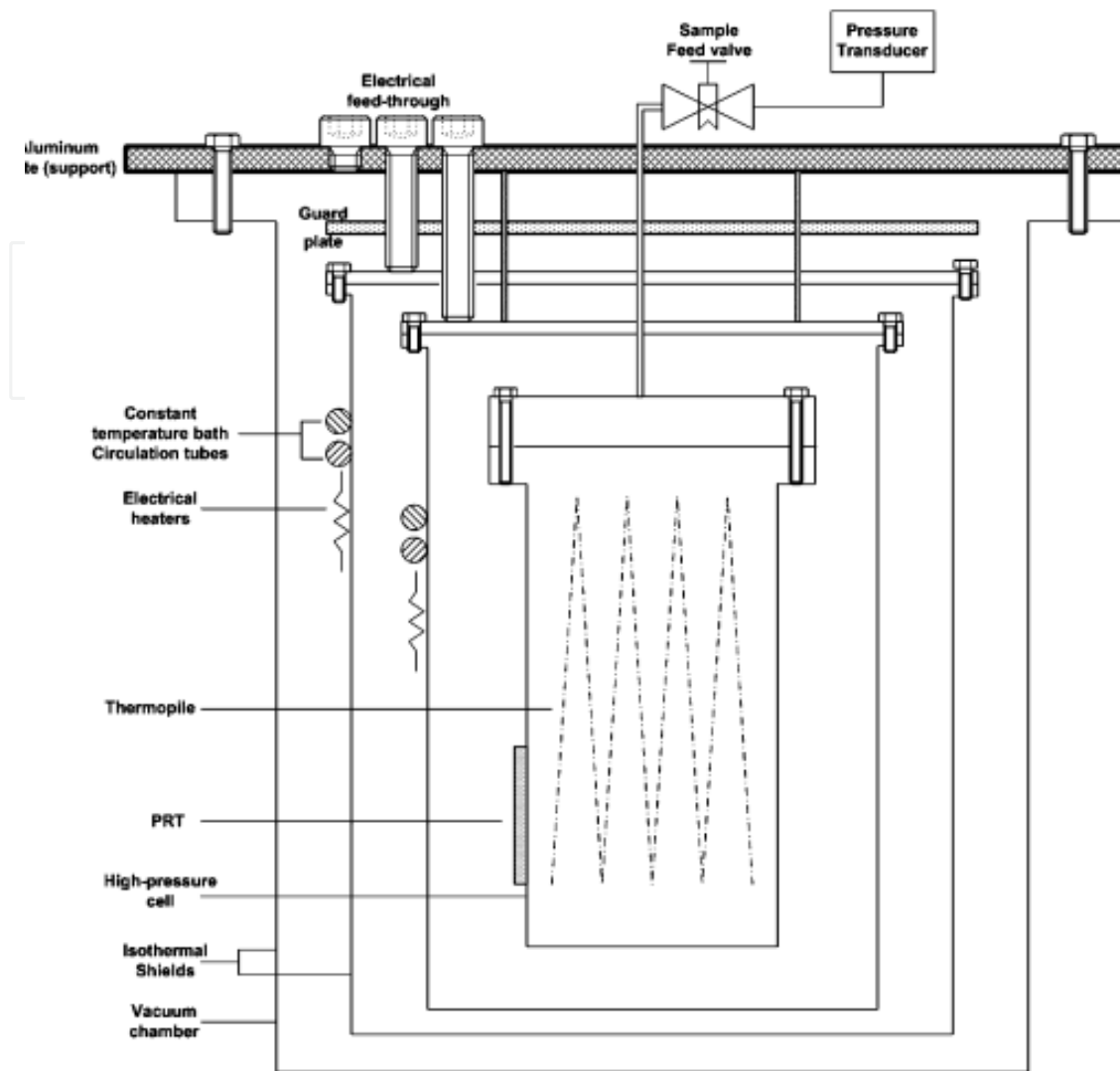
Figure 9. Scheme of isochoric cell design [65].

5. Conclusions

Techniques for the measurement of the most relevant thermophysical properties for the characterization of natural gas mixtures are reviewed showing the state-of-the-art, and the weaknesses and strengths of the current methods. Accurate determination of density, viscosity and phase equilibria are extremely important for the natural gas industry, both for technical and economical reasons, for production, processing and transportation purposes. Likewise, exploration and production using non-conventional reservoirs, including high pressure conditions, requires the accurate measurements in wide pressure-temperature ranges. Moreover, current predictive theoretical models using in the gas industry can not be used out of their tested pressure – temperature ranges, and thus, new accurate data are required to check the models performance and / or develop new theoretical predictive approaches. Therefore, this review could help to guide in the selection of the most suitable experimental approach for the determination of the required properties in wide pressure – temperature ranges.

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