Automated Isochoric Apparatus for *pVT* and Phase Equilibrium Studies of Natural Gas Mixtures

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Abstract

We have developed a new automatic apparatus for measuring phase loops and *pVT* properties of natural gas mixtures in our laboratory. Based upon the isochoric method, the apparatus can operate at temperatures ranging from 200 K to 450 K and at pressures up to 35 MPa, while providing absolute results in fully automated operation. Temperature measurements are accurate to 0.01 K and pressure measurements are accurate to 0.002 MPa. The experimental data show that prediction of the dew point curve with current equations of state is unreliable.

We also have developed a strategy that allows us, when using the above isochoric method together with a second apparatus capable of isothermal density measurements, to collect derived densities that are comparable in accuracy to those collected with a densimeter. The collection procedure and design are easy to automate.

1. Introduction

Natural gas reserves vary considerably in both composition and thermodynamic state. Accurate knowledge of the phase boundary and pressure-volume-temperature (*pVT*) behavior of these gases at pressures well above atmospheric pressure is of interest for several reasons. For example, the dew point curve of the fluid is particularly relevant to the production and transport of hydrocarbon mixtures. Dew points of natural gas mixtures are highly sensitive to the very small fractions of heavy hydrocarbons in the fluid, and prediction of the dew point curve with current equations of state (EOS) is unreliable (May *et al*. 2001). Another application that is of great economic significance relates to custody transfer of natural gases. Small differences in methods used to calculate volumetric flow rates in large scale metering can introduce large cost uncertainties (Savidge 1985). The AGA-DC92 EOS (Starling et al. 1992) is the current industry standard for natural gas custody transfer. Application of this EOS, however, is limited in temperature, pressure and composition. Given the economic value of phase behavior and *pVT* information, experimental measurement is the only sufficiently accurate means of determining the hydrocarbon dew point and density.

Phase equilibrium and *pVT* values can be measured simultaneously in an isochoric experiment (Eubank *et al*. 1985). The density for each isochore can be determined either by measuring the cell volume and the amount of charge or by measuring the density at one temperature using another apparatus (Duarte-Garza *et al*. 1995). Phase behavior is measured by locating the discontinous change in the slope of an isochore that occurs at the phase boundary.

2. Experimental

The new isochoric apparatus can operate at temperatures ranging from 200 K to 450 K and at pressures up to 35 MPa. The uniqueness of the apparatus appears in its simple and

compact design. It consists essentially of: an isochoric cell with a vacuum chamber, an isothermal shield; a pressure measurement system; an automated temperature measurement and control system; a gas manifold system; a heating and cooling system; and a vacuum system. The simple design of the isochoric apparatus allows relatively easy automation. This design provides uniformity and stability of the temperature inside the isochoric cell of ± 0.005 K or better from 200 K to 450 K.

The pressure measurement system reduces noxious volumes in the apparatus to the lowest level possible and keeps them essentially constant over wide ranges of temperature and pressure. Pressures are measured by reading the period of vibration of a quartz crystal transducer that has 0.01% accuracy and 0.0001% resolution. The transducer is connected to the sample cell through a fine diameter capillary.

3. Results and Conclusions

3.1 Apparatus Calibration and Performance Tests

Measurements on pure carbon dioxide and propane were used to verify the capabilities of the apparatus. Eight vapor pressures of carbon dioxide measured between 230 K and 290 K showed a maximum deviation of $\pm 0.04\%$ when compared to the correlation of Lemmon *et al.* (2000). Seven vapor pressures of propane measured between 270 and 340 K showed a maximum deviation of $\pm 0.07\%$ when compared to the correlation of Lemmon *et al.* (2000).

The properties of stainless steel were used to develop a correction for volume distortions with changing temperature and pressure

$$\frac{V(T,P)}{V(T_0,P_0)} = 1 + \gamma(P - P_0) + \beta(T - T_0) \tag{1}$$

where $\gamma = 2.53 \times 10^{-5}\,\mathrm{MPa}^{-1}$ and $\beta = 4.86 \times 10^{-5}\,\mathrm{K}^{-1}$

3.2 Natural gas phase boundaries and mixtures densities

The natural gas mixture compositions appear in Table 1.

Table 1. Gas mixture compositions

Component	Composition (mol %)
Nitrogen	2.031
Carbon Dioxide	0.403
Methane	90.991
Ethane	2.949
Propane	1.513
i-Butane	0.755
n-Butane	0.755
i-Pentane	0.299
n-Pentane	0.304

3.2.1 Phase boundaries Several equations of state commonly are employed in commercial software to determine the phase envelope of gas mixtures. The results are invariably different and depend upon the particular equation of state. Three equations of state commonly used for the determination of hydrocarbon phase envelopes are: Peng-Robinson (Peng. 1976), Soave-Redlich-Kwong (Soave. 1979) and Patel-Teja (1982). The natural gas dew points from this work were used to benchmark the performance of the PR SRK, and Patel-Teja equations. Results of this examination are in Figure 1. It is evident that Patel-Teja, PR and SRK equations of state cannot match all the measured data, but SRK has an advantage over the others.

3.2.2 Isochoric densities. Six isochores were measured for a natural gas mixture over a temperature range of 220 - 340 K at pressures up to 20 MPa. The base densities for each isochore were determined from isothermal densities measured with a magnetic suspension densimeter that has an uncertainty of 0.05%.

The measured densities have been compared to values calculated from AGA8-DC92 and NIST23 (Lemmon *et al.* 2004). The relative deviations appear in Figure 3. The Helmholtz model (Lemmon *et al.* 2004) developed by NIST agrees with experimental data within $\pm 0.4\%$ for temperatures between 270 K and 340 K. The AGA8-DC92 equation agrees with experimental data only within $\pm 0.7\%$.

4. Literature cited

Duarte-Garza, J.C.Holste, K.R. Hall, K.N. Marsh and B.E. Gammon, "Isochoric pVT and Phase Equilibrium Measurements for Carbon Dioxide+Nitrogen," *Journal of Chemical and Engineering Data*., **40**,704-711(1995).

Eubank, P.T., A Kregleswski, K.R Hall, J.C. Holste and H. Mansoorian, "Density of an Equimolar Mixture of Ethane and Methyl Chloride," *AIChE J.*, **31**(5), 849-856(1985).

Lemmon, E.W., M.O.McLinden, and M.L. Huber, NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP Version 7.1, National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg, 2004.

Lemmon, E.W., A.P.Peskin, M.O. McLinden, and D.G.Friend, NIST Standard Reference Database 12: Thermodynamic and Transport Properties of Pure Fluids Version 5.0, National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg, 2000.

May, E.F., T.J. Edwards, A.G. Mann, C. Edwards and R.C. Miller, "Development of an Automated Phase Behavior Measurement System for Lean Hydrocarbon Fluid Mixtures, Using Re-entrant RF/microwave Resonant Cavities," *Fluid Phase Equilibria.,***185**, 339-347(2001).

Patel, N.C. and A.S.Teja, "A New Cubic Equation of State for Fluids and Fluids Mixtures," *Chem.Eng.Sci.*, **77**(3), 463-473(1982).

Peng, D.Y. and D.B. Robinson, " A New Two-Constant Equation of State," *Ind. Eng. Chem. Fundam.*, **15**(1),59-64(1976).

Savidge, J.L., " Methodology for Development of a Highly Accurate Natural Gas Equation of State," Ph.D. Dissertation, University of Oklahoma , Norman, Oklahoma 1985.

Soave,G "Equilibrium Constants from Modified Redlich-Kwong Equation of State," *Chemical Engineering Science*, **27**,1197-1203(1979).

Starling, K.E., J.L.Savidge, Compressibility Factors of Natural Gas and Other Related Hydrocarbon Gases, AGA transmission Measurement Committee Report 8, American Gas Association, 1992.