

USE OF EQUATIONS OF STATE AND EQUATION OF STATE SOFTWARE PACKAGES

Adam G. Hawley
Darin L. George

Southwest Research Institute
6220 Culebra Road
San Antonio, TX 78238

Introduction

Determination of fluid properties and phase conditions of hydrocarbon mixtures is critical for accurate hydrocarbon measurement, representative sampling, and overall pipeline operation. Fluid properties such as compressibility and density are critical for flow measurement and determination of the hydrocarbon dew point is important to verify that heavier hydrocarbons will not condense out of a gas mixture in changing process conditions.

In the oil and gas industry, equations of state (EOS) are typically used to determine the properties and the phase conditions of hydrocarbon mixtures. Equations of state are mathematical correlations that relate properties of hydrocarbons to pressure, temperature, and fluid composition. Various software packages are available that use different equations of state to calculate a range of natural gas properties and phase conditions. This paper discusses the different equations of state that are available, the properties that can be obtained from each EOS, and practical uses of EOS software for natural gas pipeline applications.

Equations of State

Various EOS are available to calculate properties and phase conditions of hydrocarbon mixtures. Typically, the EOS are integrated into a software package that allows the user to select the equations of state to use for the calculations. Four of the most common EOS correlations are briefly discussed herein.

Peng-Robinson (PR)

The Peng-Robinson (PR) EOS (Peng and Robinson, 1976) is referred to as a cubic equation of state, because the basic equations can be rewritten as cubic polynomials in specific volume. The Peng Robinson EOS is derived from the basic ideal gas law along with other corrections, to account for the behavior of a “real” gas. The Peng Robinson EOS is very versatile and can be used to determine properties such as density, compressibility, and sound speed. The Peng Robinson EOS can also be used to determine phase boundaries and the phase conditions of hydrocarbon mixtures.

Soave-Redlich-Kwong (SRK)

The Soave-Redlich-Kwong (SRK) EOS (Soave, 1972) is a cubic equation of state, similar to the Peng Robinson EOS. The main difference between the SRK and Peng Robinson EOS is the different sets of experimental data that were used to generate the parameters for the two separate equations of state. The SRK equation of state parameters were generated from data collected prior to 1950, while the parameters for the Peng-Robinson equation of state were generated from data compiled through the early 1970s. Similar to the Peng Robinson, the SRK also can be used to determine fluid properties, phase boundaries, and phase conditions.

GERG-2008

One of the most recently published equations of state was developed at Ruhr-Universität Bochum (the University of Bochum) in Germany. This EOS is known as GERG-2008. GERG-2008 uses Helmholtz energy as a key variable to derive the hydrocarbon fluid properties. GERG-2008 can be used to determine various fluid properties specific to natural gas. GERG-2008 can also be used to calculate phase boundaries.

AGA-8, AGA-10, and API Chapter 14.2

American Gas Association Report No. 8 (AGA-8) was originally developed by Gas Research Institute. AGA-8 was developed specifically to determine compressibility of natural gas for high accuracy flow measurement applications. American Gas Association Report No. 10 (AGA-10) was later developed to build on AGA-8 by adding the ability to calculate density and sound speed. Both AGA-8 and AGA-10 were specifically designed to determine properties of natural gases only. As a result, AGA-10 cannot calculate phase boundaries. The American Petroleum Institute (API) also adopted the AGA equation of state, and has published the standard as API Chapter 14.2.

Using a Typical EOS Software Package

As discussed in the introduction, various software packages are available that allow computations to be executed using different equations of state. Many software packages allow the user to select the type of equation of state correlation that they would like to use for the calculations. Multiflash is one of many such programs that allow access to the Peng-Robison and SRK equations of state. Other equation of state software packages includes Aspen HYSIS, REFPROP, and VLEFlash, to name a few¹. The subsections that follow will outline the general steps

to using an equation of state software package. Screen shots will be presented from the Multiflash software package, however, other equation of state software packages will follow the same general steps to determine fluid properties and phase conditions.

Step 1: Define the Fluid Composition

The first step to performing a calculation using equation of state software is to define the fluid composition. Typical software packages have a library of hydrocarbons (typically through C₉+) and inert fluids to choose from to define the fluid composition. In a field application, the fluid composition is typically measured by a gas chromatograph. Figure 1 shows a screen shot of the interface used to select the components of the fluid to be analyzed. In Figure 1, components were selected that are typically found in transmission-quality natural gas.

After the general makeup of the fluid composition is selected, the molar ratio (percentage) of each component must be defined. This information is typically obtained from a gas chromatograph. Table 1 shows an example of how this information is input into an EOS software package. For most EOS software packages, the total molar ratio must add up 100% (on a percent basis) or 1 (on a fraction basis).

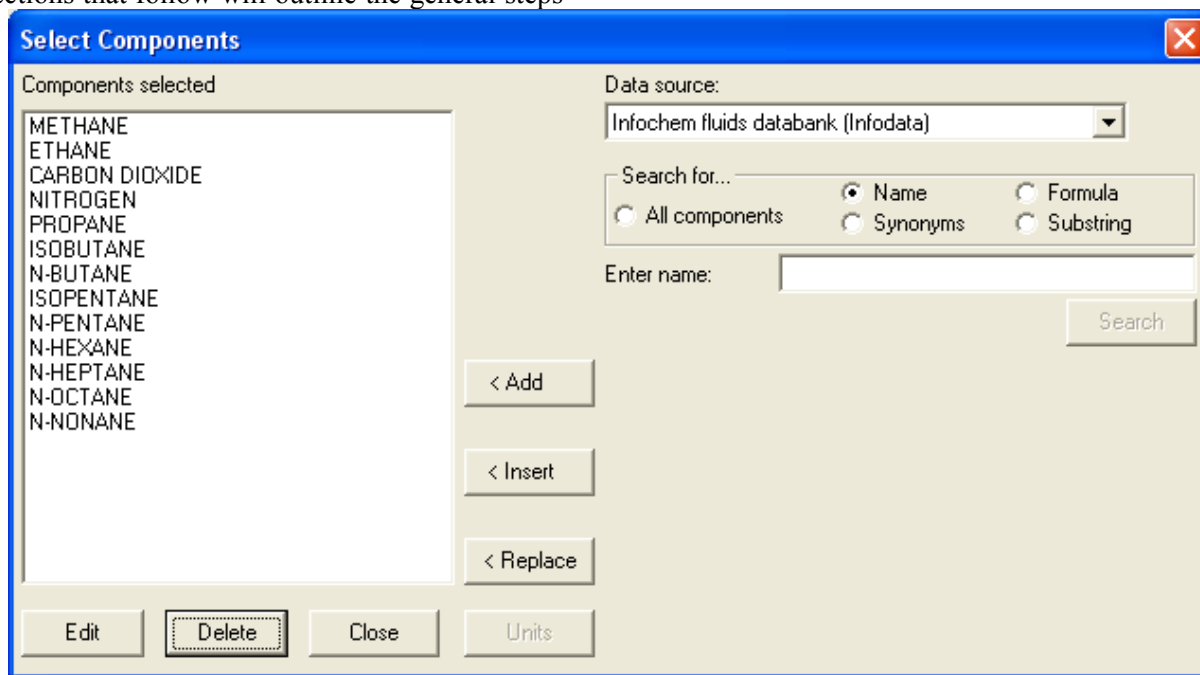


Figure 1. Selecting Components in the Equation of State Software
Components are selected that make up the fluid composition of interest.

- 1) References to trade names or specific commercial products does not represent or constitute an endorsement, recommendation, or favoring by SwRI of the specific commercial product.

Table 1. Assign the Molar Ratio of Each Component

After the components have been selected, the molar ratio of each component must be entered into the equation of state software.

Component	lbmol
METHANE	75.000
ETHANE	12.500
CARBON DIOXIDE	0.400
NITROGEN	2.800
PROPANE	6.000
ISOBUTANE	1.000
N-BUTANE	1.600
ISOPENTANE	0.180
N-PENTANE	0.240
N-HEXANE	0.146
N-HEPTANE	0.068
N-OCTANE	0.048
N-NONANE	0.018

Step 2: Select Type of Calculation

After the fluid composition has been defined, the next step is to select the type of calculation that will be executed. Three different types of calculations are discussed in this paper: 1) flash calculations, 2) single-phase property calculations, and 3) phase diagrams.

Flash calculations can be used to determine the phases of the fluid and the fluid properties of all phases present. Flash calculations are useful if it is unknown whether or not the fluid will be single or multiphase at the given state. Typical flash calculations are defined by the two properties that define the state. For a flash calculation, two of the following six variables must be fixed:

- Temperature
- Pressure
- Density
- Enthalpy
- Entropy
- Internal Energy

Flash calculations at constant pressure and temperature are the most common, because these properties are the most readily available in a field application.

A single-phase property calculation can be done on single-phase fluids only, such as the gas calculations

performed by AGA-10. In a single-phase property calculation, it is assumed that the fluid is single-phase.

In addition to flash calculations and single-phase property calculations, some EOS software can also determine the phase diagram of a fluid. This can be very helpful in the field to determine if a phase change will occur due to a change in temperature and/or pressure of the process fluid. Phase diagrams will be discussed in more detail later in this paper under “Practical Uses of EOS Software”.

Step 3: Define Flash Conditions

With the fluid composition and type of calculation defined, the fluid conditions for the calculation must be defined. Based on the chosen calculation type, different fluid conditions will need to be entered in the software. For the constant pressure and temperature flash condition, the pressure and temperature of the fluid will need to be defined. Likewise, for the constant pressure and enthalpy case, the pressure and enthalpy will need to be defined, and so on. The units for the defined conditions are specified in the EOS software package.

For generating a phase diagram, the fluid conditions are not required. Instead, the EOS software iterates through a range of pressures and temperatures to define the curve of the phase diagram. A starting pressure and temperature can be defined for the iteration to help expedite the calculation, but it is not required

Step 4: Perform the Calculations and Review the Results

With all the parameters defined, a flash calculation or a phase diagram can be created. Figure 2 shows the results of a flash calculation at a fixed pressure and temperature of 40 °F and 100 psi. In Figure 2, it can be seen that a range of fluid properties have been calculated at the defined conditions.

In addition to the fluid properties, the flash calculation has indicated that two phases are present at the defined conditions. The EOS software supplies fluid properties for the liquid and the gas phase as well as the amounts of each phase at the defined conditions. For the example at 40 °F and 100 psi, the fluid is more than 99.9% gas with trace amounts of liquid (~0.0643%).

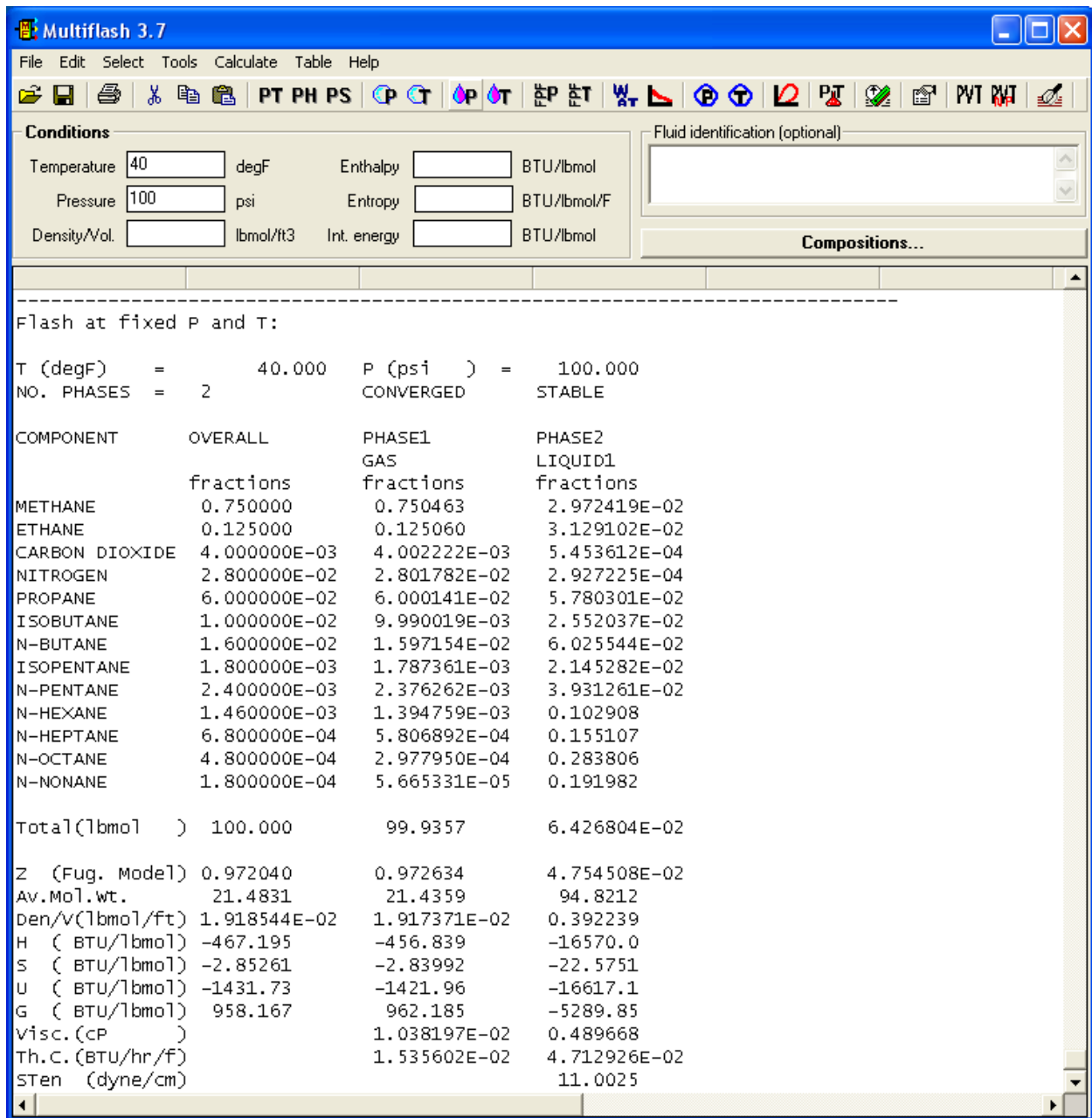


Figure 2. Results from a Fixed Pressure and Temperature Flash Calculation

At the defined conditions, the flash results show that the fluid has two phases. Properties for both the liquid and gas phases are given by the flash calculation.

Practical Uses of EOS Correlations

Two example cases are discussed in this paper to illustrate situations where equation of state correlations can be used in field applications: 1) to verify sound speed measurements for an ultrasonic meter and 2) to check if the conditions through a sample line could cause liquid to condense out of the gas phase.

Sound Speed Verification

Ultrasonic meters measure fluid velocity to determine the flow rate of a process fluid through a pipeline. In addition to fluid velocity, ultrasonic meters also measure the sound speed of the process fluid. As a result, comparing the sound speed measured from an ultrasonic meter to the calculated sound speed, using an equation of state correlation,

is a good method to verify that an ultrasonic meter is functioning properly.

AGA-10 is a good option for sound speed determination, since it is the standard in the natural gas industry. Following the steps that were previously outlined, the composition must first be defined. A gas chromatograph is the most common option to obtain the compositional makeup of the gas in the field. Keep in mind that the accuracy of the properties, determined by an equation of state correlation, are only as good as the input information that is used to determine the gas properties. As a result, it is important to check and verify the compositional information of the process fluid before it is used to calculate properties that will be used for analysis.

After the composition of the fluid is defined, the type of analysis and the conditions must also be defined. For the AGA-10 equation of state, the fixed pressure and temperature condition is used to calculate properties of the fluid (including sound speed). Once the temperature, pressure, and gas composition are entered into the AGA-10 equation of state, the calculation can be initiated and the properties of the gas, at the given conditions, will be determined. The sound speed determined from AGA-10 can then be compared to the sound speed measured by an ultrasonic meter. If there is a discrepancy in the sound speed, it could be due to the flow meter. Keep in mind, however, that if the pressure, temperature, or compositional data that were used to determine the fluid properties are biased, the bias will also be present in the calculated fluid properties.

Liquid Condensate in Sample Line

As discussed earlier, equation of state correlations can be used to determine phase boundaries and generate phase diagrams. This information can be especially useful in field applications with natural gas sampling. A phase diagram can be used to determine if liquids could condense out of the gas due to a change in the pressure and/or temperature during the sampling process. Natural gas sample

lines typically contain a regulator that drops the pressure of the gas from the pipeline pressure to a lower level that a gas analyzer can accept. If liquids condense out of the gas phase in a gas sample, equipment downstream from the sample location could be damaged. In addition, if liquids condense out of the gas phase, the composition of the remaining gas sample will be compositionally distorted from the actual gas that was sampled. This could cause a discrepancy in the gas properties determined from the gas samples.

A phase diagram can be generated using equation of state software that references PR, SRK, or GERG-2004 equation of state. AGA-10 was designed for single-phase gas only and cannot be used to generate phase diagrams.

To generate a phase diagram, the composition of the natural gas is required. Using the composition that was previously displayed in Table 1 and using the SRK equation of state, the calculated phase diagram in Figure 3 was generated. The liquid, two-phase, and gas regions have been labeled in Figure 3.

Figure 3 shows an example of a condition in which liquids could be generated in a sample line. Assume that point 1 on Figure 3 is the process pressure and temperature of a natural gas pipeline (1000 psi and 100 °F). Also assume that a gas analyzer was connected to the pipeline that required a 200 psi inlet pressure. If a regulator was installed that dropped the pressure from 1000 psi to 200 psi without heating, then the gas would follow the line from point 1 to point 3. At point 3, the pressure is 200 psi, however, the gas has cooled to approximately 44°F due to Joule Thomson cooling. As a result, the gas in the sample lines would be two-phase as some of the heavier hydrocarbons would have started to condense out of the gas phase. Ideally, the path from point 1 to point 2 would maintain the fluid in the gas phase. To obtain the path from point 1 to point 2, a heater can be installed on the sample line to offset the Joule-Thomson cooling effect and maintain the temperature of the gas above the dew point line in Figure 3.

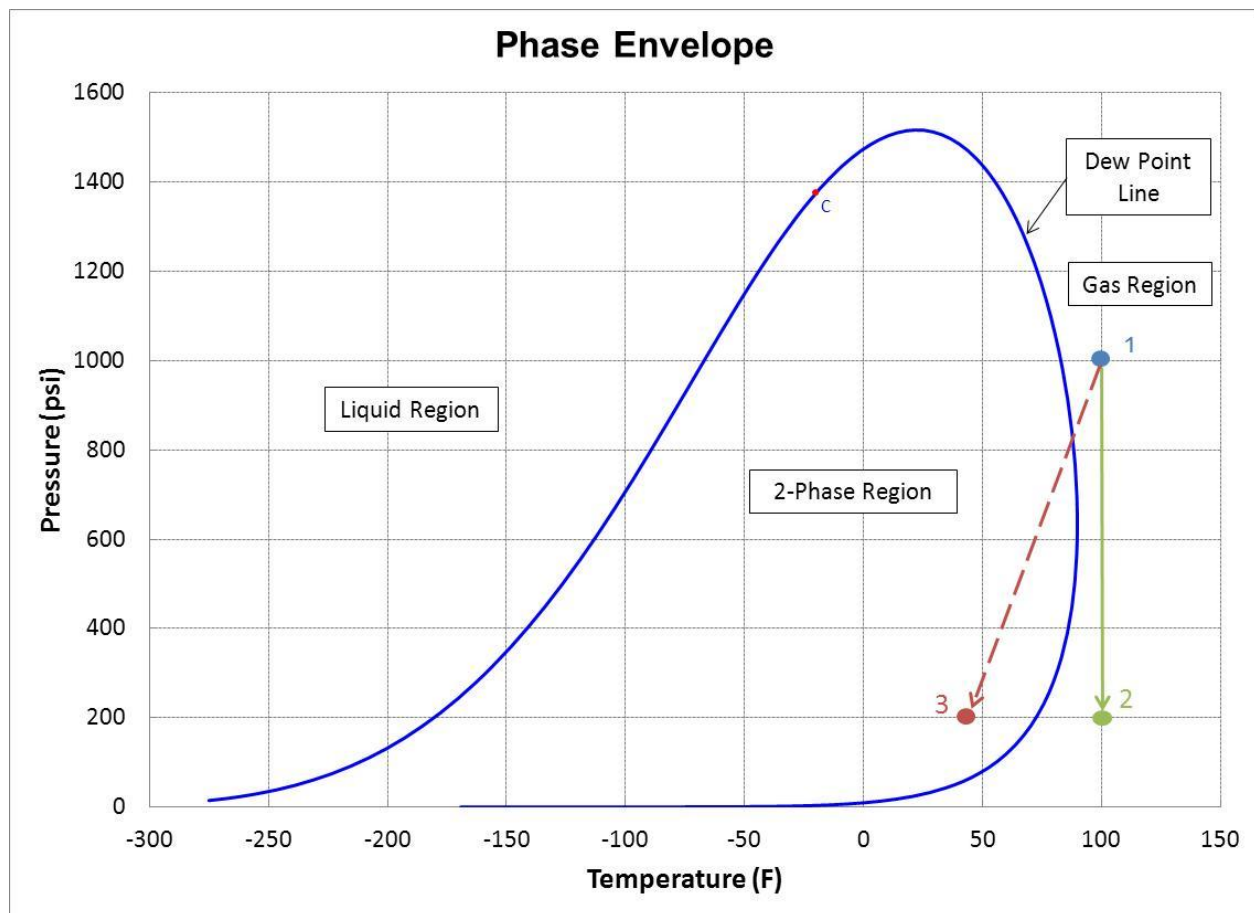


Figure 3. Phase Diagram Results Using SRK Equation of State

The liquid, two-phase, and gas regions are labeled in the figure. The green path from paths 1-2 represent an ideal isothermal pressure drop with heating, while the path from 1-3 represents a realistic drop in pressure taking into account the drop in temperature from Joule-Thomson cooling.

Comparison of Gas Properties from Different EOS Correlations

This paper has discussed four different EOS correlations that can be used to determine properties of natural gas. Since all of the EOS correlations use data that was derived from different experiments, it is expected that slightly different fluid properties will be obtained from each EOS correlation for identical input conditions. This begs the question of which EOS correlation should be used? For natural gas measurement, AGA-10 is the standard for computing properties. All flow calculations for natural gas refer to the AGA-10 equation of state. Table 2 shows an example of the difference between the AGA-10, SRK, and Peng-Robison EOS for a density calculation for natural gas at 800 psi, 100°F using the composition previously outlined in Table 1. In Table 2, it can be seen that differences ranging from -1% to 2.2% were observed for the SRK and PR EOS in comparison to AGA-10. As a

result, it is important to use the correct EOS correlation for fluid calculations, especially if they are to be used to high-accuracy flow measurement. AGA-10 should be used for all natural gas property determination for flow measurement, unless otherwise noted in tariff agreements.

Table 2. Density Results from AGA-10, SRK, and PR Equation of State Correlations

The SRK equation of state and PR equation of state yielded density results -1% and 2.2% different from AGA-10, respectively.

Equation of State	Density (lbm/ft ³)	Percent Difference
AGA-10	3.3729	--
SRK	3.3386	-1.0%
PR	3.4456	2.2%

Conclusions

Equation of state correlations can be valuable tools in the natural gas industry to determine properties of gas and phase boundaries. Many different software packages are available that allow a straight-forward approach to applying and comparing the different equation of state correlations. Knowing the advantages and limitations of the available equations of state is very useful in deciding which correlation is best suited to determine phase boundaries or fluid properties.

As discussed throughout this paper, equations of state are only as good as the data that is input into the correlations. As a result, if high accuracy determination of fluid properties and phase boundaries is critical, verify the inputs into the equation of state correlations (pressure, temperature, composition, etc.) before the calculations are carried out.

References

American Gas Association, AGA Report No. 8, *Compressibility Factors of Natural Gas and Other Related Hydrocarbon Gases*, Second Edition, Second Printing, American Gas Association, Arlington, Virginia, 1994.

American Gas Association, AGA Report No. 10, *Speed of Sound in Natural Gas by Multipath Ultrasonic Meters*, Second Edition, American Gas Association, Arlington, Virginia, April 2007.

Kunz, O., Klimeck, R., Wagner, W., and Jaeschke, M., *The GERG-2004 Wide-Range Equation of State for Natural Gases and Other Mixtures.*, GERG TM 15, 2007.

Mayeaux, M., *Use of Equation of State (EOS) Software*, ASGMT Presentation, September 2011.

Peng, D.Y., and Robinson, D. B., "A New Two-Constant Equation of State," *Industrial and Engineering Chemistry Research Fundamentals*, Vol. 15, pp. 59-64.,1976.

Savidge, J., *Compressibility of Natural Gas*, ISHM Presentation, May 2012.

Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," *Chemical Engineering Science*, Vol. 27, pp. 1197-1203, 1972.

Adam Hawley



Darin George

