

Equation of State Tutorial

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14 September 2000

Introduction

As the art of pipeline flow simulation has advanced, the rigor and, we trust, the accuracy of the many elements making up a flow model have increased. Steady-state models have given way to transient solutions, fluid properties are calculated and tracked along the pipeline, and configurations are represented in more detail. Isothermal models have been replaced with solutions of the energy flow equation supported by real-fluid thermodynamics and ground heat flow models. Accurate fluid properties and thermodynamics require accurate equations of state.

There are many more equations of state than could be reasonably discussed in a single paper. This tutorial reviews current practice using equations of state in the simulation of fluid flow in pipelines, starting with fundamental considerations, following with a discussion of several ancient & modern equations of state, and concluding by discussing what's reasonable to use. *Reasonable* is a subjective word, and the decisions as to which equations to consider and which to use for what are based on the author's experience in simulating the flow of gases, liquids, supercritical fluids, two-phase systems, on preferences arising from that experience, and on externally imposed requirements.

What's an Equation of State?

An equation of state is a relationship between *state variables*, such that specification of two state variables permits the calculation of the other state variables. There are many state variables; usually in fluid dynamics we talk about pressure, temperature, and density because these variables appear in the equations of motion.

Examples of equations of state are, for gases, the ideal gas law:

$$P = \frac{\rho RT}{M} \quad (1)$$

where P is the pressure, psia
 ρ is the density, lb/cu ft
 R is the gas constant, psia-cu ft/deg R-pound-mole
 T is the absolute temperature, deg R
 M is the molecular weight

For liquids, we have the bulk modulus equation:

$$\rho = \rho_o \left(1 + \frac{(P - P_o)}{\beta} \right) \quad (2)$$

where β is the bulk modulus, psi
and the subscript o indicates a reference condition.

We also have for liquids a thermal expansion equation:

$$\rho = \rho_o [1 - \alpha(T - T_o)] \quad (3)$$

where α is the thermal expansion coefficient, deg^{-1}

These ideal gas and liquid equations work reasonably well over limited temperature and pressure ranges for many substances. However, pipelines commonly operate outside these ranges and may move substances that are not ideal under any conditions. We will examine the limitations on these ideal equations of state, and present some equations of state with wider validity.

A Little Scientific Background

One of the first equations of state for gases was *Boyle's Law*:

$$\frac{V}{V_o} = \frac{P_o}{P} \quad (4)$$

where V is the gas volume,
 P is the pressure,
and the subscript, o , refers to initial or standard conditions.

Boyle's law expresses the observation that the volume of a gas decreases as the pressure increases. Boyle's law is only part of an equation of state, since it only involves two variables. The second part is *Charles' Law*:

$$\frac{V}{V_o} = \frac{T}{T_o} \quad (5)$$

where T is the absolute temperature.

Charles' law expresses the observation that gases expand as they are heated.

Charles' law contains a couple of significant concepts:

- *Absolute Temperature* – Actually, the original form of Charles law had the temperature replaced by the temperature plus a constant. The constant was later determined to be absolute zero in whatever temperature units were being used.
- *Zero Volume Molecules* – Since the volume goes to zero at absolute zero (according to Charles law) the molecules must have zero volume. The correctness, or lack thereof of this concept will become important as we examine equations of state.

The combination of Boyle's and Charles' laws, plus another conceptual jump, gives a form of the ideal gas law:

$$PV = nRT \quad (6)$$

where n is the number of *moles* of gas

Equation (6) is the formulation of the ideal gas law favored by chemists. It becomes equation (1) by defining density as:

$$\rho = \frac{nM}{V} \quad (7)$$

What Do We Want from an Equation of State?

In pipeline flow simulations we use equations of state for the following:

- Determine the density from the temperature & pressure for:
 - Linepack calculations
 - Flowmeter calibration
 - Pressure drop calculations
- Determine thermodynamic variables for;
 - Thermal modeling
 - Compressor calculations
 - Vapor-liquid equilibrium

These uses imply certain characteristics of an effective equation of state:

- Accuracy (<0.1% for custody transfer flow meters)
- Applicable over wide temperature and pressure ranges
- Applicable over wide range of compositions
- Rigorous (for thermodynamics; Not quite the same thing as accuracy)
- Works for liquids too
- ***Easy to use !!!***

There is usually a contradiction between the last characteristic and the others.

How does the Ideal Gas Law Stack Up?

The ideal gas law was originally developed in the form of equation (6), rather than equation (1) because it is easier to measure gas volumes than gas densities, and because chemists tend to think in terms of moles rather than masses. Although the ideal gas law was originally derived from Boyle's law and Charles' law, it can also be obtained from the kinetic theory of gases.

Getting the ideal gas law from the kinetic theory of gases requires a couple of assumptions which give us some insight into the physics:

- The gas molecules occupy no volume, which was already implied by Boyle's law.
- There are no forces between the molecules except at the instant of collision.

For a gas at atmospheric (standard) conditions, these two assumptions are nearly satisfied. There is so much space between the molecules that the forces between the molecules are only significant when they are very close compared to the average distance between them, and the volume is nearly all comprised of empty space. One thing I learned in freshman chemistry was that a gram-mole of gas occupies 22,400 cubic centimeters at atmospheric conditions. If the gas is water, a gram-mole is 18 grams. The density of liquid water is 1 gram/cubic centimeter, so the volume of the liquid is 18 cubic centimeters. Since the molecules of a liquid nearly fill up all the space, the molecules of a mole of gaseous water at atmospheric conditions occupy less than 1/1000 of the total gas volume.

The average distance between these molecules is the cube root of 22,400 divided by Avogadro's number, 6.02×10^{23} , which works out to be a bit over 10^{-6} centimeters. This is a rather small distance, but the range of the intermolecular forces is about 10^{-8} centimeters. Therefore, for a gas under standard conditions, the distance between the molecules is nearly always beyond the reach of the intermolecular forces.

Looking at the ideal gas law in the context of the list of desirable characteristics, we have:

- Accuracy – Good at low densities (generally low pressures and/or high temperatures)
- Temperature and pressure ranges – Not good near dew point or critical point
- Composition range – All composition effects are in the molecular weight
- Rigor – Not so good: The Joule-Thompson effect, which is caused by intermolecular forces, is zero for ideal gases.
- Liquids – Hopeless: For a liquid, the basic assumptions don't even come close. The molecules of a liquid are always in contact with one another, and are always under the influence of forces exerted by their neighboring molecules. This is why liquids are very difficult to compress.
- **Easy to use !!!** – A winner!

The pressure limitation alone is enough to drive a requirement for better equations of state for pipelines.

Somewhat Better Gas Laws

Van der Waals

We will consider the Van der Waals equation of state for the following reasons:

- Its historical interest
- It is based on a better physical understanding of how gases work
- It provides a useful improvement for some gases and conditions
- Some of the modern, more accurate equations of state (SRK and PR) are based on it

It was observed early on that the gas law didn't quite work for higher pressures and lower temperatures. Van der Waals determined that the effect of the long range forces and the volume occupied by the molecules was approximately accounted for by the equation:

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad (8)$$

where: a, b are constants, known appropriately as the *Van der Waals* constants.

It should be fairly obvious that b is a volume and is, approximately, the volume of a mole. The term $V - nb$ is the free volume the molecules have to run around in.

It may not be quite so obvious that $\frac{n^2 a}{V^2}$ corresponds to an attractive force between molecules. This attractive force makes the pressure less than it would be for an ideal gas, hence the positive sign.

The Van der Waals equation works reasonably well for pressures below 200 psi and temperatures above 0 deg F, provided that the gas isn't close to condensing. It's being used successfully right now for a low pressure HCl gas pipeline.

I was amused to see a note in a handbook saying: *It is known that a and b vary to some extent with temperature.*! This comment obviously dates from a time when high pressures and/or very low temperatures didn't often occur.

The Van der Waals equation can be expressed in terms of density by substituting

$$\rho = \frac{nM}{V} \text{ from equation (7):} \quad \left(P + \frac{n^2 a}{\left(\frac{nM}{\rho}\right)^2}\right)\left(\frac{nM}{\rho} - nb\right) = nRT \quad (9)$$

Which, with a little manipulation, simplifies to:

$$\left(P + \frac{a\rho^2}{M^2}\right)\left(\frac{M}{\rho} - b\right) = RT \quad (9a)$$

The Universal Gas Law

The universal gas law is:
$$P = \frac{z\rho RT}{M} \quad (10)$$

where z is the compressibility, dimensionless.

Note: We sometimes talk about the super-compressibility, F_v . z is related to the super-compressibility, by the equation: $Z = \frac{1}{(F_v)^2}$.

The wonderful thing about the universal gas law is that it will describe any gas; you just need to know the value of z . The not-so-wonderful thing is that determining z can be quite a chore, and z varies with pressure and temperature. The universal gas law does not solve the problem of obtaining an accurate equation of state over a large range of pressures and temperatures. It recasts the problem into the determination of z .

There are a couple of advantages to the universal gas law:

- One is that the value of z is a measure of how far the gas is from ideality. At atmospheric conditions, the value of z is typically around 0.99. Under pipeline conditions, the value is typically around 0.9. For condensed hydrocarbons, the value is typically less than 0.5.
- Another advantage is that the universal gas law can be used in model and thermodynamic calculations based on the ideal gas law, with z and the thermodynamic quantities themselves determined from a better equation of state in a separate process.

The Gas Constant

We have discussed several equations of state in which the gas constant, R , appears. The gas constant is a universal constant of nature, whose value depends on the units used. Note that the units of the gas constant are always energy/deg-mole, which happens to be the same as those of molar specific heat.

One handbook gives values of the gas constant for 84 sets of units. The table below gives a few values, sometimes used in pipelines.

Gas Constant, R	Pressure Units	Volume Units	Temperature Units	Moles
10.7335	psia	cu ft	Deg R	lb-moles
1545	psfa	cu ft	Deg R	lb-moles
8.314	pascals	cu m	kelvins	g-moles
8314.4	pascals	cu m	kelvins	kg-moles
83,144	bar	cu m	kelvins	kg-moles

The Virial Equation of State

The virial equation of state is:

$$PV = \left[1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \dots \right] nRT \quad (11)$$

This equation is rather obviously similar to a Taylor's series expansion in $1/V$. Again the problem has been reformulated into finding the temperature dependent coefficients B, C , etc. These coefficients themselves may be expanded in power series in temperature. The number of coefficients tends to get out of hand. About 20 years ago an equation of state of the virial type was published which had 28 constant coefficients, which was still inaccurate as the gas approached condensation. However, we shall see even more coefficients.

What Makes a Good Equation of State?

A good equation of state should be simple, accurate, and should cover a wide range of pressures, temperatures, and compositions. Such an equation of state does not exist. There are equations of state that are accurate over large ranges of pressure and temperature, even near the dew point or critical conditions. They are not simple! And changing the composition means changing the equation of state, which is another involved process.

For natural gas pipelines, we want equations of state that are accurate over the conditions and compositions over which gas pipelines operate. Furthermore, we would like to be able to handle composition changes in a straightforward way.

Special Pipeline Equations of State

For natural gas transmission pipelines in the United States, the gas quality, or the composition, is usually kept within a range that permits the use of equations of state of moderate complexity. Examples of such equations of state are NX-19 (AGA-3) and the AGA-8 gross characterization method.

For pipelines there are two somewhat different applications, which may affect the choice of equation of state:

- *Custody Transfer* – Although physical accuracy is important, the legal and financial aspects of custody transfer applications impose a primary requirement that the parties agree on the equation of state to be used. In the past this requirement has led to the use of “standard” equations or procedures even when there were known inaccuracies. Fortunately, the current AGA recommended equations are accurate as over the range of gas quality, pressures, and temperatures used for transmission pipelines in the U.S.
- *Simulation* – Accurate simulations require equations of state that are physically accurate. For such fluids as LPG’s and ethylene, and for gas gathering operations equations of state with a wider range of applicability are required to support accurate simulations.

There have been a series of special pipeline equations of state developed over the years: NX-19, Sarum, and the two AGA-8 equations. These equations of state have progressively improved in physical accuracy over the range of pressures, temperatures, and compositions occurring in U.S. transmission pipelines. They have tended to be almost purely empirical

The AGA-8 Equation of State

There are actually two AGA-8 equations of state, called the *detail* characterization method and the *gross* characterization method.

The AGA-8 detail characterization method equation of state is:

$$P = dRT \left[1 + Bd - D \sum_{n=13}^{18} C_n^* T^{-u_n} + \sum_{n=13}^{58} C_n^* T^{-u_n} (b_n - c_n k_n D^{k_n}) D^{b_n} \exp(-c_n D^{k_n}) \right] \quad (12)$$

where d is the molar density of the gas

B is the second virial coefficient ($C(T)$ in equation (11))

$D = \rho / \rho_c$ is the reduced density

C_n^* are coefficients which are functions of the composition

u_n, b_n, c_n, k_n are constants.

The AGA-8 gross characterization method equation of state is:

$$P = dRT \left[1 + B_{mix} d + C_{mix} d^2 \right] \quad (13)$$

where B_{mix}, C_{mix} are the second & third virial coefficients, respectively. The *mix* subscript indicates that the calculation of the virial coefficients for the mixture does not consider the detailed composition, but considers hydrocarbons collectively (as an *equivalent hydrocarbon*) plus terms for CO₂ and nitrogen.

The AGA Transmission Measurement Committee Report No. 8: *Compressibility Factors for Natural Gas and Other Related Hydrocarbon Gases* (1992) gives constants, recommended pure gas parameters, and mixing rules for equations (12) and (13).

NX-19 Equation of State

The NX-19 equation of state was used for many years for transmission gas pipelines until it was replaced by better equations. It is more of a procedure than what we normally think of as an equation. The procedure is found in the 1962 AGA Manual for the Determination of the Supercompressibility Factors for Natural Gas: *PAR Research Projecy NX-19 "Extension of Supercompressibility Tables"*. This paper compares NX-19 results with other equations of state, primarily so that those still using NX-19 can get an idea of the discrepancies.

Real-Fluid Equations of State

Real-Fluid means that the equation of state has no idealizations such as are used in the ideal gas law, the bulk modulus equation, the thermal expansion equation, or even the Van der Waals equation. Since no one has been able to develop an equation of state valid near critical or dew points from first principles, this means that such equations are largely based on empirical fits to data.

In principle, given enough data and a willingness to do a lot of uninspiring but difficult work, the accuracy of an empirical fit, and the complexity of the system described are unlimited. For example, the USCGS puts out an empirical fit based on a spherical harmonic expansion of the Earth's magnetic field that covers the entire earth, including the effects of iron ore bodies, etc. There are 600 terms in the equation.

The AGA-8 detail characterization method uses an equation of state with 58 coefficients, which are determined from 58 sets of 10 parameters, plus several parameters for each component, plus a mixing parameter for each pair of components. (They've almost caught up with the USCGS!) The equation still doesn't work for liquids, or near critical conditions.

We will consider three widely used equations of state that do work reasonably well near the dew point, and for both liquids and gases: Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), and Benedict-Webb-Rubin-Starling (BWRS). In addition to covering a wide range of conditions, these equations also can be expressed in generalized forms with *mixing rules* that permit the calculation of the coefficients for different compositions. For this reason these equations, and AGA-8 are sometimes called *compositional* equations of state.

SRK and PR, along with the Van der Waals equation, are called *cubic* equations of state, because expansion of the equations into a polynomial results in the highest order terms in density (or specific volume) being cubic, or third power terms. BWRS adds fifth & sixth power and exponential density terms.

The cubic equations are all of the form:

$$P = \frac{RT}{V-b} + \frac{a}{V^2 + AV + B} \quad (14)$$

If V is the molar volume and A and B are zero, (14) becomes the Van der Waals equation, (8). For the more general equations, a, b, A and B are functions of temperature which must be determined from empirical fits to the data.

The Soave-Redlich-Kwong (SRK) Equation of State

The SRK equation is a modification by Soave of the Redlich-Kwong (RK) equation, which had been widely used for chemical equilibrium calculations. The SRK equation produces better liquid densities, although BWRS is even better. For the SRK equation, B in equation (14) becomes zero, and $A = b$. a and b are given by:

$$a = \frac{0.42748 R^2 T_c^2}{P_c} \left[1 + (0.48 + 1.574\omega - 0.176\omega^2) (1 - T_r^{0.5}) \right]^2 \quad (15)$$

$$b = \frac{0.08664 R T_c}{P_c} \quad (16)$$

where ω is a measure of the gas molecule's deviation from spherical symmetry called the *Pitzer acentric factor*

$T_r = T/T_c$ is the *reduced temperature*

and the subscript, c , refers to critical conditions.

The numerical constants and the T_r dependence are selected so as to produce fits to hydrocarbon vapor pressures.

From equation (16) the Van der Waals interpretation of b as the volume of the molecules says that the molecules occupy about 1/12 of the gas volume at critical conditions.

With a and b from (15) and (16), the SRK equation is:

$$P = \frac{RT}{V - \frac{0.08664 R T_c}{P_c}} + \frac{\frac{0.42748 R^2 T_c^2}{P_c} \left[1 + (0.48 + 1.574\omega - 0.176\omega^2) (1 - T_r^{0.5}) \right]^2}{V^2 + \frac{0.08664 R T_c}{P_c} V} \quad (17)$$

Many workers have produced variations on the SRK equation of state involving fits (by adjusting the numerical constants) to other sets of data, and even modifying the form of the temperature dependence. These variations will not be addressed here.

Equation (15) may be expressed in terms of density with $V = M/\rho$:

$$P = \frac{\frac{\rho R T}{M}}{1 - \frac{0.08664 \rho R T_c}{M P_c}} + \frac{\frac{0.42748 \rho^2 R^2 T_c^2}{M^2 P_c} \left[1 + (0.48 + 1.574\omega - 0.176\omega^2) (1 - T_r^{0.5}) \right]^2}{1 + \frac{0.08664 \rho R T_c}{M P_c}} \quad (17a)$$

The Peng-Robinson (PR) Equation of State

In the PR equation of state, $A = 2b$, $B = -b^2$,

$$a = \frac{0.45724R^2T_c^2}{P_c} \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5}) \right]^2 \quad (18)$$

and
$$b = \frac{0.07780RT_c}{P_c} \quad (19)$$

so that the PR equation is:

$$P = \frac{RT}{V - \frac{0.07780RT_c}{P_c}} + \frac{\frac{0.45724R^2T_c^2}{P_c} \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5}) \right]^2}{V^2 + 2\frac{0.07780RT_c}{P_c}V - \left(\frac{0.07780RT_c}{P_c} \right)^2} \quad (20)$$

where, again, the numerical constants were obtained by fits to hydrocarbon vapor pressure data.

In terms of density, equation (20) becomes:

$$P = \frac{\frac{\rho RT}{M}}{1 - \frac{0.07780\rho RT_c}{MP_c}} + \frac{\frac{0.45724\rho^2 R^2 T_c^2}{M^2 P_c} \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5}) \right]^2}{1 + 2\frac{0.07780\rho RT_c}{MP_c} - \left(\frac{0.07780\rho RT_c}{MP_c} \right)^2} \quad (20a)$$

Limitation on Cubic Equations of State

Van der Waals, SRK, and PR have the common problem that they are not adequate at high densities, either for liquids or supercritical fluids. The reason lies in the nature of the intermolecular force. At distances greater than the typical separation between molecules in a liquid, the force is attractive, and changes as rather low power of the distance between molecules. Once the molecules are in contact, the force becomes repulsive, and increases exponentially as the distance decreases. This is another way that saying that the molecules are incompressible. Pushing the molecules closer together requires deforming the molecules, which they resist strongly.

Representing the rapid increase in the repulsive intermolecular force with distance requires a dependence on density which is stronger than a cubic relationship.

One way to get the stronger dependence is to carry the virial equation (11) out to more terms. The problem is that many terms are required. In addition to the complexity, a large number of coefficients to be evaluated from the data can make the resulting function less general.

The BWRS equation avoids this problem by adding exponential terms, in addition to higher order density terms.

The Benedict-Webb-Rubin-Starling (BWRS) Equation of State

The BWRS equation is a modification of an equation of state first published by Benedict, Webb & Rubin (BWR) in 1940. The density dependence of BWR is retained in BWRS; the temperature dependence of the coefficients is changed. In 1973 Starling wrote a book, **Fluid Thermodynamic Properties of Light Petroleum Systems**, Gulf Publishing Co. with BWRS coefficients for light hydrocarbons, mixing rules for determining coefficients for mixtures of hydrocarbon gases, and with procedures for determining thermodynamic quantities and for vapor/liquid equilibrium calculations.

Probably because of its ability to cover both liquids and gases and the availability of coefficients and mixing rules for many hydrocarbons in one place, BWRS is probably the most widely used equation of state for simulation of pipelines with high density hydrocarbons, or with condensation. In one application on a liquid ethane pipeline, the ethane flashed into a gas in part of the pipeline due to an upset condition. The real-time model, using the BWRS equation of state, continued to simulate the flow in the part liquid, part gas pipeline and even detected a leak test that happened to be under way during the upset.

Simplicity is not among the good qualities of the BWRS equation of state. The form of the equation is:

$$P = \frac{\rho RT}{M} + \left(B_o RT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4} \right) \frac{\rho^2}{M^2} + \left(bRT - a - \frac{d}{T} \right) \frac{\rho^3}{M^3} + \alpha \left(a + \frac{d}{T} \right) \frac{\rho^6}{M^6} + \frac{c\rho^3}{M^3 T^2} \left(1 + \frac{\gamma \rho^2}{M^2} \right) \exp \left(- \frac{\gamma \rho^2}{M^2} \right)$$

Where the eleven coefficients, $A_o, B_o, C_o, D_o, E_o, a, b, c, d, \alpha$ and γ , must be determined empirically. Values of the coefficients may be determined either by fitting data for the gas of interest, or by calculation from the composition using mixing rules, critical properties of the pure compounds, and the generalized coefficients provided by Starling.

Once the coefficients are known for the fluid of interest, all state variables can be calculated from two known state variables. Unfortunately, many flow models determine pressure and temperature from the flow equations, leaving the density to be determined from the equation of state. Since BWRS is implicit in density, an iterative density calculation is required. Profilers run on flow models using BWRS usually show that the model is spending most of its time in the density calculation routine.

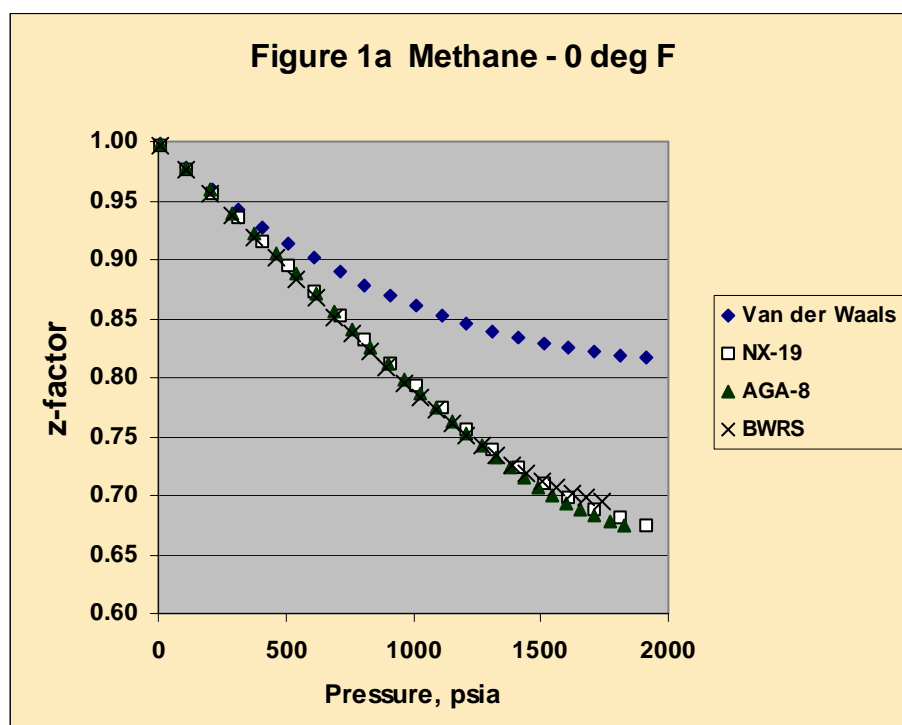
Equations of State for Mixtures

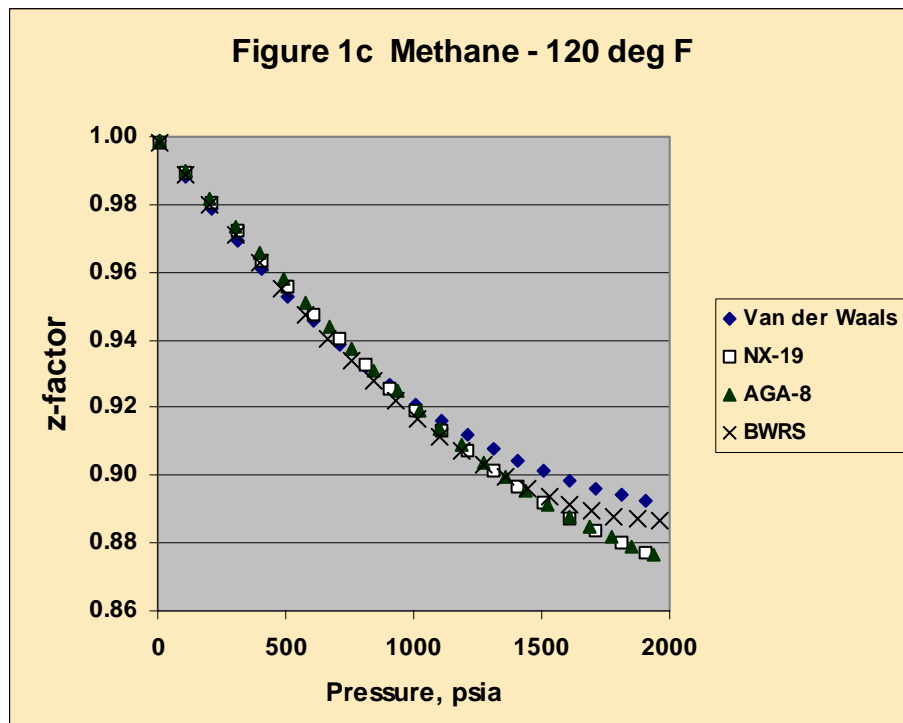
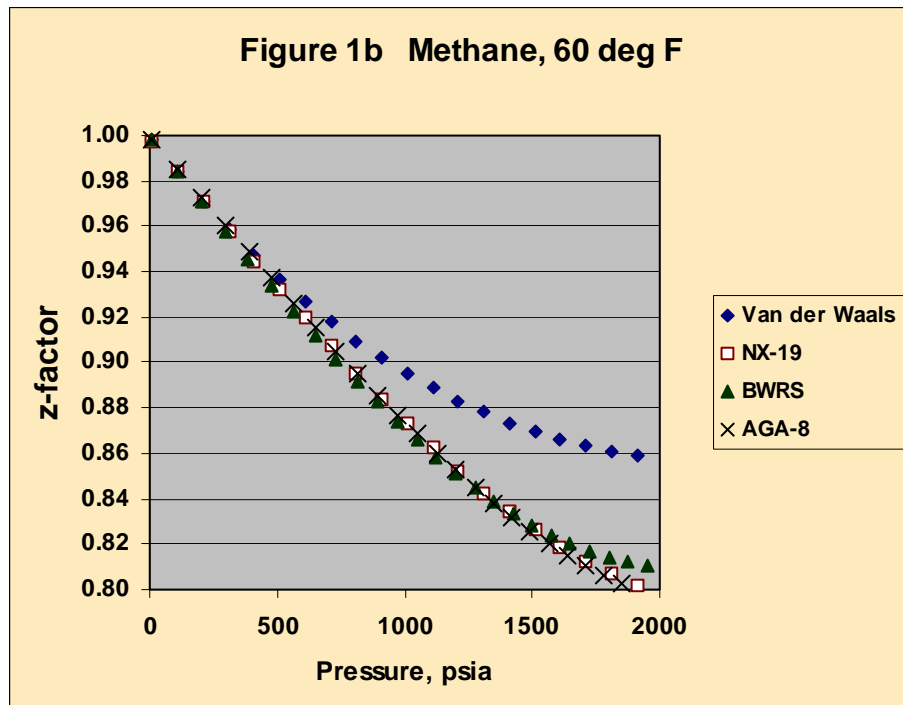
The SRK and PR equation as given are for pure compounds. Mixing rules for determining the effective critical properties for mixtures are given in **The Properties of Gases and Liquids** by Reid, Prausnitz, and Poling.

Starling (1973) provides detailed mixing rules for determining coefficients for the BWRS equation.

Results from Selected Equations of State

Equations of state are most easily compared in terms of the compressibility, z . The fractional difference in the calculated standard volumes is the same as the fractional difference in z for two equations. In Figure 1, Van der Waals, NX-19, AGA-8 (detailed characterization) and BWRS are compared for pure methane over a range of pressures at 0, 60, and 120 deg F.





It can be seen that NX-19 and AGA-8 agree well over the entire range. BWRS agrees with the NX-19 and AGA-8 up to about 1500 psia. As expected, Van der Waals agrees with the

other equations at low pressures. At high pressures, Van der Waals is off because of the inadequacy of a single parameter in representing the effect of the intermolecular forces.

At this point it's worthwhile to discuss the source of the NX-19, AGA-8 and BWRS coefficients. NX-19 and AGA-8 are empirical fits to a large number of pressure/density/temperature measurements for gases of pipeline quality. The significant meaning of "pipeline quality" for equation of state is that the heavy hydrocarbon and water contents are limited.

The BWRS coefficients used herein are primarily based on empirical fits to vapor-liquid equilibrium data for pairs of components over a large range of compositions. Generally, PR and SRK coefficients are also based on vapor-liquid equilibrium data.

In view of the data upon which they are based, it is no surprise that NX-19 and AGA-8 do not work very well for gases near condensation. It is, perhaps, more of a surprise that BWRS works so well for gases far from condensation.

Effects of Composition

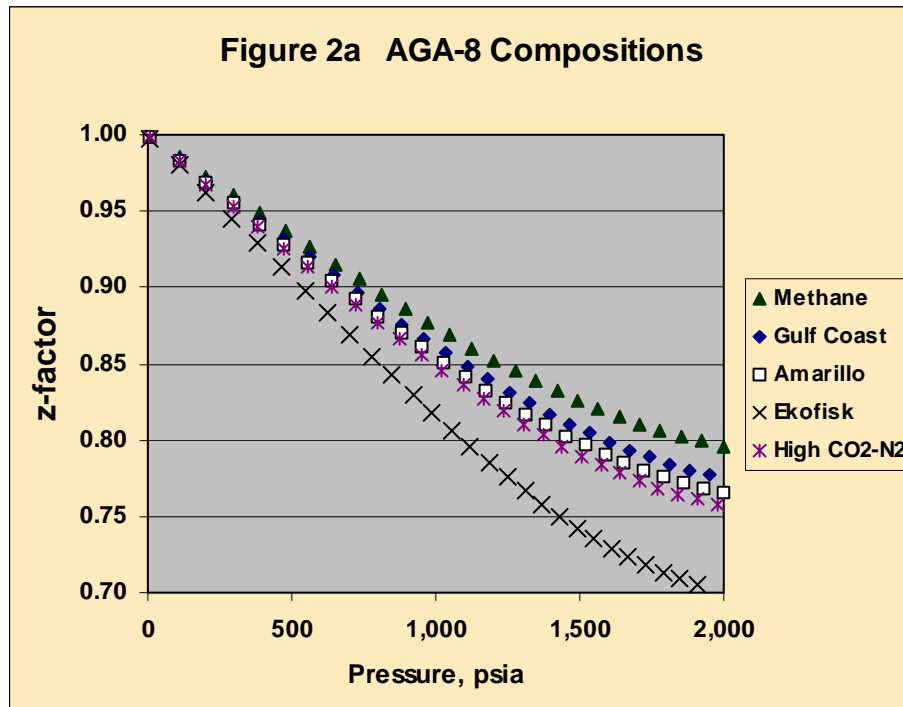
Effects of Composition

Generally, heavier hydrocarbon molecules are larger and have a greater affinity for one another. Both of these factors make heavier hydrocarbons deviate more from an ideal gas.

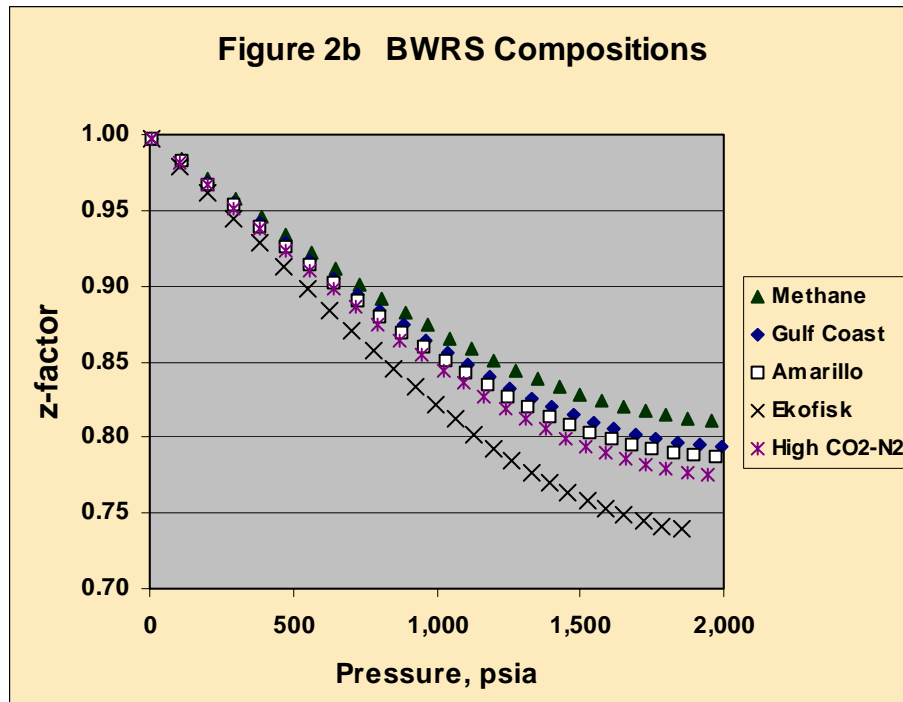
The AGA-8 report gives the compositions of several natural gases for reference purposes. Table 1 gives the compositions for some of these gases, with components heavier than butane added to the n-butane mole percent.

Component	Gulf Coast	Amarillo	Ekofisk	High CO ₂ -N ₂
Methane	96.5222	90.6724	85.9063	81.2110
Ethane	1.8186	4.5279	8.4919	4.3030
Propane	0.4596	0.8280	2.3015	0.8950
i Butane	0.0977	0.1037	0.3486	0.1510
n Butane	0.2468	0.2720	0.4495	0.1530
N ₂	0.2595	3.1284	1.0068	5.7020
CO ₂	0.5956	0.4676	1.4954	7.5850

Figure 2 shows results from AGA-8 and BWRS for these gases. The SRK and PR give results similar to BWRS.



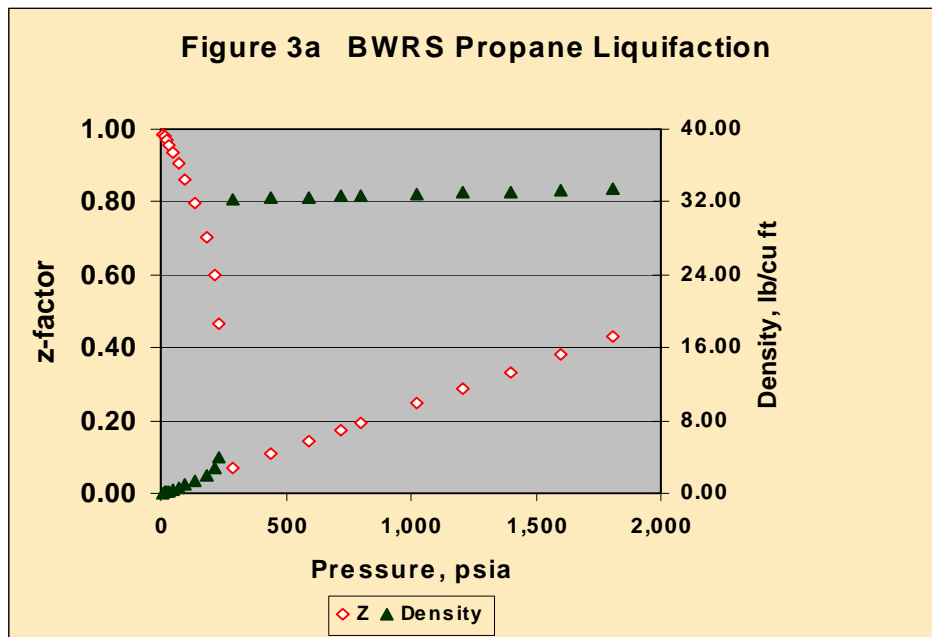
The general trend is lower compressibilities (deviations from ideality) as the proportion of



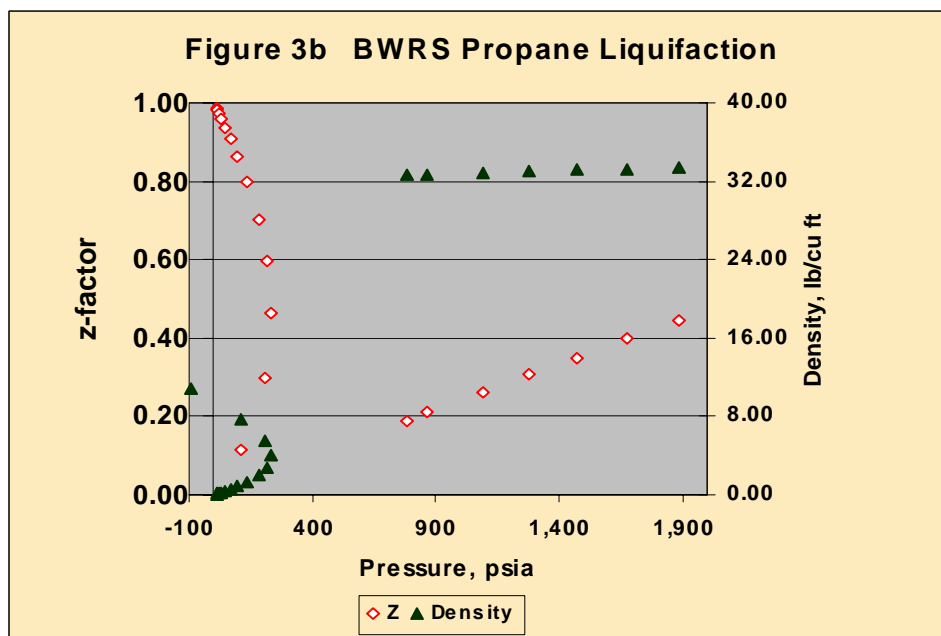
heavier components increase. This result is to be expected, because the heavier molecules have a greater attraction for one another. Because the C5+ components were lumped in with n-butane, the figures slightly under estimate this effect.

Condensation

A major reason for using BWRS, PR, or SRK is their applicability near condensation conditions. BWRS results for propane are shown in Figure 3.



It can be seen that the BWRS equation gives results through the condensation region. However, a



Caveat is in order, as can be seen in Figure 3b. The results are nearly the same as in 3a, with the addition of points within the density range 4-30 lb/cu ft. The behavior of the curve is strange, even going to a negative pressure. This is because these densities are not possible for propane at this temperature (60 deg F). However, the equation of state, which

is an empirical fit, will calculate a pressure for any density given it. Care must be taken to reject invalid densities.

Conclusions

Ideal equations of state are generally inadequate for custody transfer conversions or for accurate pipeline flow simulations. Accurate equations of state are available; they tend to be complex. There are two types of state equations, differing in how the coefficients are fitted to data. The equations recommended by AGA (NX-19, AGA-8) are fitted directly to pressure/temperature/density data over the range of conditions and compositions commonly found in U.S. transmission pipelines. SRK, PR, and BWRS are fitted to vapor/liquid equilibrium data.

Generally, the AGA equations are more accurate for normal transmission pipeline conditions and compositions. SRK, PR, and BWRS cover a wider range of conditions. They are expected to be more accurate for gathering systems operating close to condensation.

For a transmission pipeline using an AGA equation for flow meter conversions and SRK, PR, or BWRS for a simulation model, the differences between the equations should not be significant, in view of the uncertainties in other pipeline parameters, in particular, the temperature profile along the pipeline.

SRK, PR, and BWRS are valid for liquid hydrocarbons as well as gases, and can be used to determine vapor/liquid equilibrium. In the condensation region, for pure compounds care is needed not to force non-physical densities intermediate between gases and liquids. For mixtures in the condensation region, the mixture compensation itself may be non-physical. That is, no single fluid exists at that composition under those conditions. The fluid separates into a liquid and a gas, either of which has the mixture composition. In such a case, the vapor/liquid equilibrium must be determined, and two-phase flow must be taken into account.

All of the available real-fluid equations are implicit in density, so that calculation of the density from the pressure & temperature requires iterative methods. This fact argues for formulating the flow equations in terms of density rather than pressure. However, at boundaries with measured pressures, iterative calculations of boundary densities will still be required. Perhaps someone will take on the labor of re-formulating one of the equations of state in with density as the dependent variable.

Biography

Jerry L. Modisette, Ph. D.

Dr. Modisette is an independent pipeline software consultant, currently working with Energy Solutions International (formerly LICEnergy and Wright-Logue Associates).

Dr. Modisette started his professional career with NASA, where he worked on boundary layer diffusion, solid rocket design, and astrophysics. During the Apollo program he was Chief of the Space Physics division at NASA MSC in Houston where he was responsible for protection of the astronauts from space radiation hazards.

In 1969 Dr. Modisette became a professor of physics, associate dean, & research director at Houston Baptist University. In 1971, while in academia, he began development of pipeline technology, beginning with leak detectors based on rarefaction waves, and culminating with the first real-time pipeline simulator installed in 1978. He also worked in other fields, patenting inventions for measurement of properties of drilling fluids, generation of energy from ocean waves, vapor recovery, and refrigeration.

In 1980 he left the university to develop pipeline applications software full time. He was one of the founders and the provider of technology for a series of companies, *CRC Bethany International*, *Real Time Systems*, and *Advanced Pipeline Technologies (APT)*. During this time he developed much of the simulation and applications technology that form the basis of the industry today. He also trained many of the people who are now leading consultants, technologists, or managers in the industry.

In 1992 he founded *Modisette Associates, Inc.*, which took over the business of *APT*. *Modisette Associates* operated successfully, doing major pipeline applications projects in North America. These projects included replacing the model and leak detection system he had installed on a Canadian pipeline in 1978 with updated technology. This pipeline, running a Modisette real-time model from 1978 to the present, is the longest record of continuous operation of a pipeline model in the world.

In 1998, *Modisette Associates* was acquired by *LICENERGY, Inc.*, where Dr. Modisette was Chief Scientist until January 2000.

Other developments by Dr. Modisette include:

- The first transient pipeline model with an accurate thermal model. (1979)
- The first transient two-phase flow model, featuring physically based, continuous flow regime transitions, and rigorous vapor-liquid equilibrium calculations. (1982)
- The first real-time model to calculate the mixing by turbulent diffusion of products at a batch interface. (1978)

Education:

B. S. (Mathematics) Louisiana Polytechnic Institute, 1956

M. S. (Physics) Virginia Polytechnic Institute, 1960

Ph. D. (Space Science) Rice University, 1967