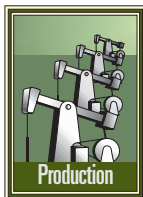


A study on predicting acid-gas densities for the pressure and temperature ranges relevant to acid-gas injection schemes found that only one common equation of state gave unsatisfactory results.



Studied were the Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), Patel-Teja (PT) equations as well as the effect of volume shifting on the SRK and PR equations. The study included pure hydrogen sulfide (H₂S) and carbon dioxide (CO₂) and mixtures of the two.

The study found that SRK equation was unsatisfactory for predicting densities over the entire range of conditions because errors for this equation were often greater than 10%.

The volume-shifted SRK is marginally satisfactory. The volume-shift dramatically improves the density in the liquid region but not in the supercritical region. The other four equations (PR, two volume shifted PR, and PT) exhibited errors less than 10%, except in the near critical region.

Knowledge of densities of these gases is important for designing acid-gas injection schemes.

Acid-gas injection

Acid gas is a byproduct of natural gas sweetening processes. It is toxic and environmentally problematic and must therefore be dealt with appropriately.

For large quantities of acid gas, operators typically use a Claus process to convert the H₂S in the gas to elemental sulfur and release the CO₂ to the atmosphere. But for small acid-gas quantities, injection has become an economical way to deal with the acid gas. Furthermore, acid-gas injection is a low-emission process, much lower than a Claus plant.

Western Canada currently has about 25 such projects in operation and several more in the planning stages. This disposal method also is starting to be looked upon favorably in other parts of the world.

One should note that acid-gas injection is not limited to small projects. Sulfur prices currently are low and elemental sulfur stockpiling may not be

an option for sulfur producers. Limited space may force them to find alternatives for disposing of large quantities of acid gas by such means as injection.

Acid-gas injection is a simple concept. The acid gas from the amine regenerator tower is at a low pressure, typically less than 200 kPa (29 psi), and at about 50° C., the temperature of the overhead condenser. It also is saturated with water.

Multi-stage compressors compress the gas to the pressure required for injecting it

into a deep reservoir. Surface pressure usually is substantially less than the reservoir pressure because of the hydrostatic head of the fluid being injected. Injection pressures depend on the injection zone and may be as great as 15 MPa (2,176 psi). Reservoir pressure can be 30 MPa or higher.

One key parameter in the design of an acid-gas injection scheme is fluid density.^{1,2} Needed are accurate density predictions for the vapor, liquid, and supercritical (dense-phase) regions.

This article reviews the available experimental data for acid-gas densities and examines several popular methods for density calculations. Density prediction methods that are phase specific will not be examined. For example, there are several correlations designed for estimating the liquid densities.³

In acid-gas injection, it is important to predict the density for all fluid phases. It is also important to have a well-behaved function as the fluid transverses the various phase regions.¹ The liquid density correlations, therefore, are less useful for this application, even though they are accurate.

**OIL & GAS
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Study determines best methods for calculating acid-gas density

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There is a large amount of experimental data available for CO₂ and H₂S densities. Therefore, this article includes only literature reviews. These compilations cover the pure component properties over the range of pressure and temperature of interest in this study.

For acid-gas injection, the temperature of interest is from 0° to 150° C. and the pressure of interest is from atmospheric to 30 MPa.

Pure CO₂

Literature provides significantly

SIX REGIONS FOR PURE COMPONENTS

Table 1

| | Reduced temperature | Reduced pressure |
|-------------------------|-------------------------------------|---|
| 1. Liquid region | $T_r < 0.95$ | $P_r > P_r(\text{sat})$ |
| 2. Vapor region | $T_r > T_r(\text{sat})$ | $P_r < P_r(\text{sat})$ or $P_r < 0.9$ |
| 3. Near critical region | $0.95 < T_r < 1.05$ | $0.9 < P_r < 1.5$ |
| 4. Supercritical region | $T_r > 0.95$ | If $0.95 < T_r < 1.05$ then $P_r > 1.5$ If $T_r > 1.05$ then $P_r > 0.9$ |
| 5. Saturated liquid | $T_r = T_r(\text{sat}), T_r < 0.95$ | $P_r = P_r(\text{sat})$ |
| 6. Saturated vapor | $T_r = T_r(\text{sat}), T_r < 0.95$ | $P_r = P_r(\text{sat})$ |

CO₂ DENSITY ERRORS

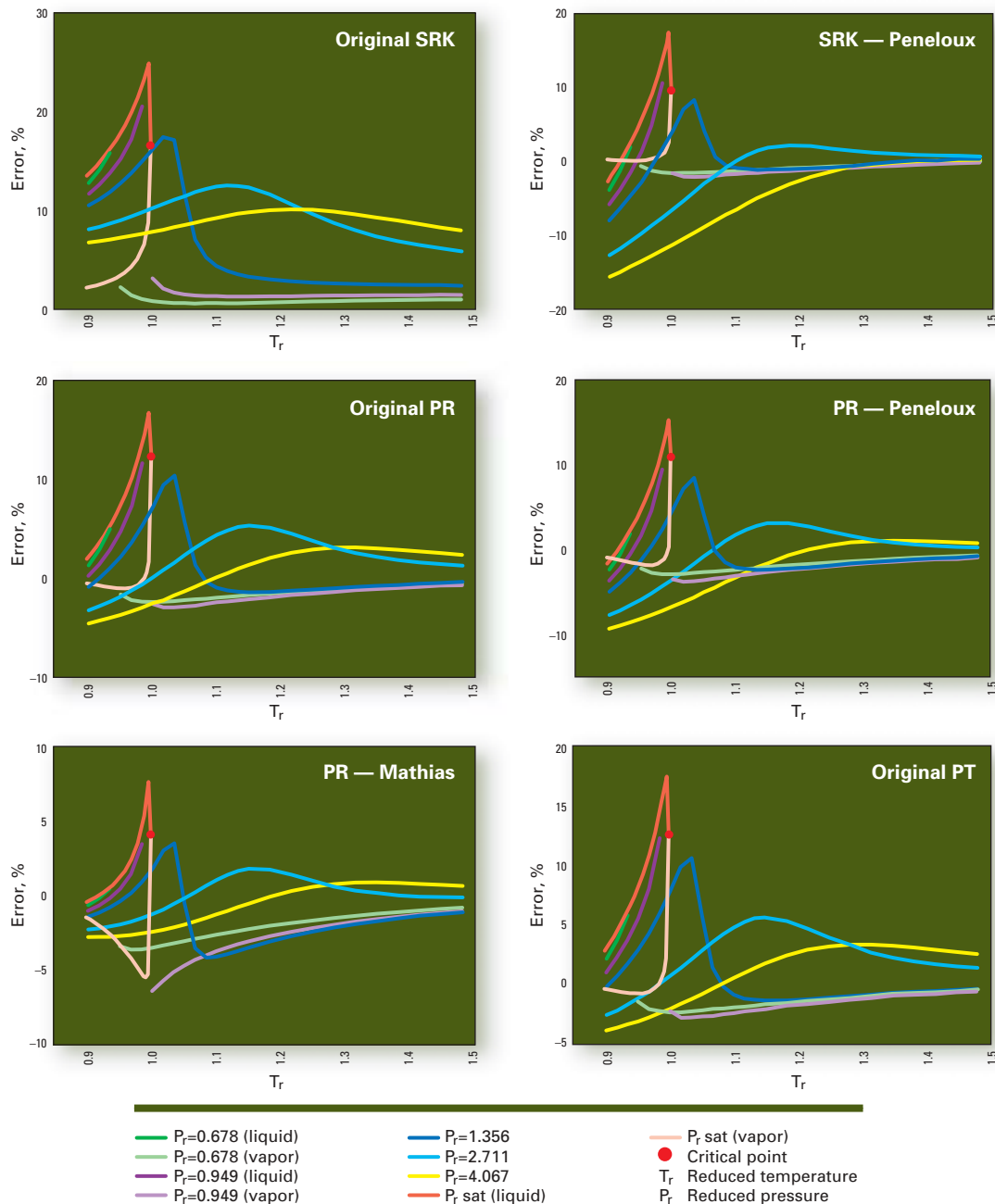


Fig. 1

CO₂ thermodynamic properties and formulated several tables, and Vukalovich and Altunin⁶ reviewed both CO₂ thermodynamic and transport properties. Although their data sets are useful, they have been superseded by the newer tables of Span and Wagner.

Pure H₂S

Goodwin⁷ extensively reviewed H₂S thermodynamic properties. He used an advanced equation of state to construct a table of properties over a wide pressure and temperature range, which was used in the study discussed in this article.

The correlation for H₂S has much less data than for CO₂, but nevertheless, the Goodwin tables are probably the best currently available for H₂S thermodynamic properties.

Binary mixtures

Robinson⁸ (see also Macrygeor⁹) studied the phase behavior and volumetric properties of sour gas mixtures and reported the densities

for three CO₂ and H₂S mixtures: 17.75%, 20.35% and 60.25% of H₂S at 71.1° C. and pressures from 1.0 to 12.4 MPa. All these data are in the gaseous region with compressibility factors ranging from 0.95 to 0.45.

Kellerman¹⁰ in a more thorough investigation of the H₂S plus CO₂ binary system measured the densities of four mixtures: 6.07%, 9.55%, 29.33%, and 49.99% H₂S. Temperatures ranged from -23.2° to 176.9° C. and pressures were

more data on CO₂ than for H₂S, particularly for transport properties. One reason is that CO₂ is considerably easier to deal with than H₂S. In addition, CO₂ has a much lower critical point, placing this interesting region in a range more accessible to experimenters.

The vicinity near the critical point attracts researchers because the physical properties in that region have properties which change dramatically with small changes in either temperature or

pressure.

Span and Wagner⁴ provide the latest review of the thermodynamic properties of CO₂. Their investigation is a thorough and critical review of the available experimental data. The tables generated use a highly accurate but complex equation of state. The study discussed in this article uses their tabulation to compare model density predictions.

Angus⁵ also thoroughly reviewed

up to 20.0 MPa. These measurements included both liquid and vapor regions.

The study discussed in this article used data from both Robinson and Kellerman.

Modeling acid-gas density

In process modeling, equations of state, mostly cubic equations of state, are the models of choice. This is particularly true for simulation processes for natural gas treatment.

Two popular cubic equations are the Soave¹¹ modification of the Redlich-Kwong equation (SRK) and the Peng and Robinson¹² (PR) equation of state. Literature contains additional modifications of these equations. In fact, commercial software packages often implement the modifications under the original names; therefore, the software user should be cautious.

Literature classifies PR and SRK equations as two-parameter, cubic equations. These equations can show significant deviations in predicted liquid density when compared to experimental data. Errors are typically on the order of 5-10%, although larger errors can be expected in the region near a critical point.

Recent attempts at improving liquid density calculations employ higher-order equations. For example, the Patel and Teja¹³ (PT) model has three parameters, and the Trebble^{14,15} (TBS) model has four parameters.

These higher-order equations rarely improve the vapor-liquid equilibrium compared to the predictions from the simpler two-parameter models, and

H₂S DENSITY ERRORS

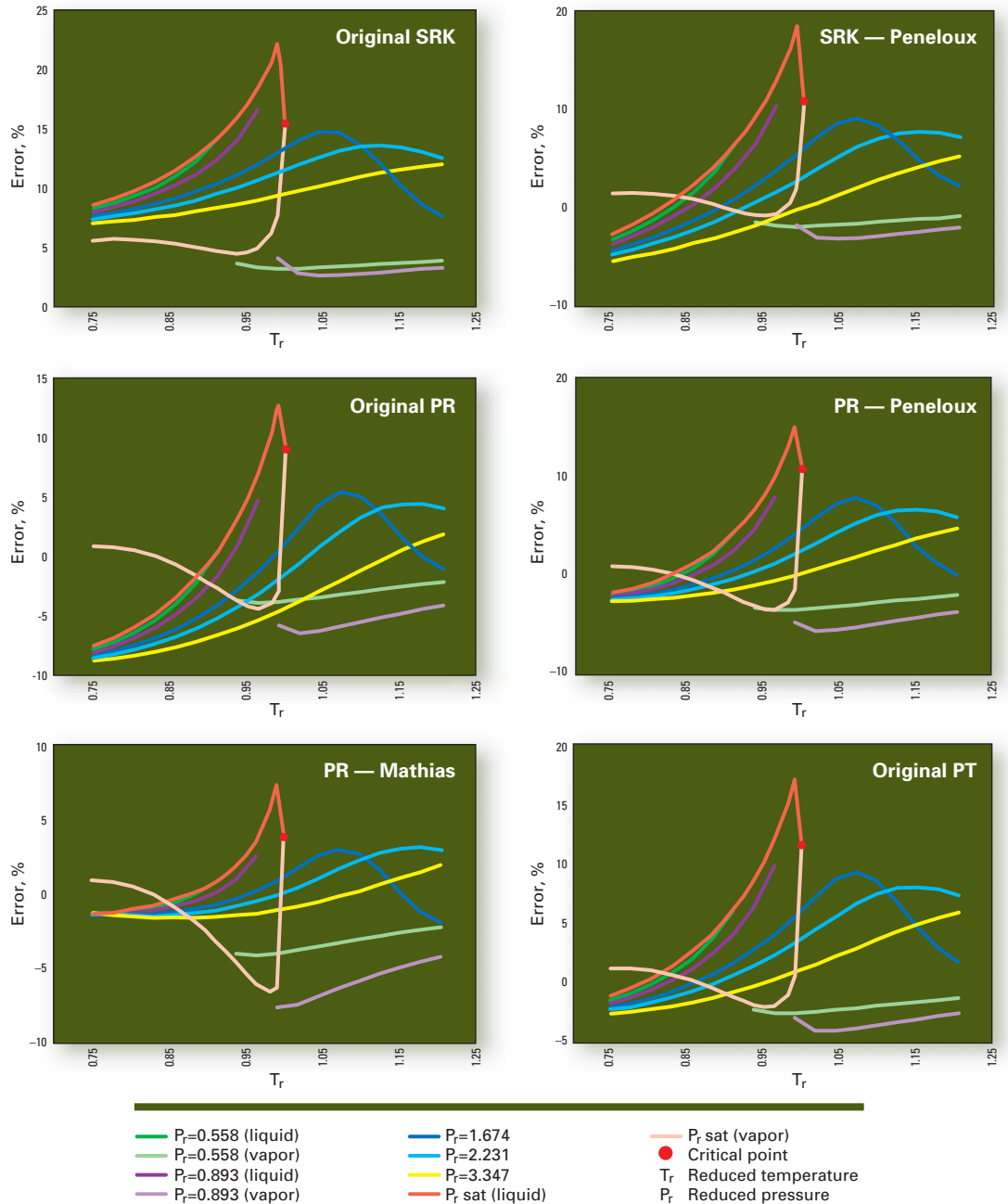


Fig. 2

therefore have not gained wide acceptance because of their added complexity.

This study focuses on PR, SRK, and PT equations of state for predicting acid-gas density in the vapor, liquid, and dense-phase regions. The accompanying box describes the component properties and summarizes the three equations of state.

Density

Equations of state relate the temper-

ature, pressure, and specific (or molar) volume of a fluid. Cubic equations of state model the pressure of a fluid as a sum of an attractive and repulsive term. The equations are therefore in the form $P = f(T, v)$.

Rearrangement of the equations to a volume explicit form produces a cubic, third-order, polynomial. The solution to a cubic equation result in one real or three real roots, of which two or all three may be equal.

EQUATIONS OF STATE

Component properties

Equation of state models require the critical point and acentric factor as pure component input parameters. The data used in this study are as follows:

| | | | |
|---|---|---------|--|
| Carbon dioxide , (Span and Wagner ⁴) | | | |
| Critical temperatures, K | — | 304.128 | |
| Critical pressure, Mpa | — | 7.3773 | |
| Acentric factor | — | 0.22491 | |
| Molecular weight, g/mol | — | 44.0098 | |

| | | | |
|---|---|---------|--|
| Hydrogen sulfide , (Goodwin ⁷) | | | |
| Critical temperatures, K | — | 373.40 | |
| Critical pressure, Mpa | — | 8.9629 | |
| Acentric factor | — | 0.09578 | |
| Molecular weight, g/mol | — | 34.0758 | |

The study derived the acentric factor of the pure components from the vapor pressure data and the basic definition of the acentric factor:

$$\omega = -\log(P_r^{\text{sat}} @ T_r = 0.7) + 1$$

For CO₂, this involved extrapolating the vapor pressure expression. The triple point of CO₂ is 216.59 K, which is a reduced temperature of 0.7122.

According to the method of Peneloux,¹⁶ the volume shift parameter should be obtained by fitting the saturated liquid density at $T_r = 0.7$. This study obtained the shift parameters by minimizing the AAE for the saturated liquid density over the following temperature ranges:

$$\begin{aligned} \text{CO}_2: & 0.898 < T_r < 0.950 \\ \text{H}_2\text{S}: & 0.732 < T_r < 0.950 \end{aligned}$$

The lower reduced temperature corresponds to 0° C., the lowest temperature of interest in this study. For the SRK, the study used the following Peneloux-type volume shift parameters:

$$\begin{aligned} c_{\text{CO}_2} &= -8.6650 \text{ cc/mole} \\ c_{\text{H}_2\text{S}} &= -3.3826 \text{ cc/mole} \end{aligned}$$

And for the PR equation the following parameters:

$$\begin{aligned} c_{\text{CO}_2} &= -1.7493 \text{ cc/mole} \\ c_{\text{H}_2\text{S}} &= +2.2176 \text{ cc/mole} \end{aligned}$$

For the Mathias-type correction to the PR equation, the study obtained the s parameter by fitting the saturated liquid density at $T_r = 0.7$ (or nearly so). The v_c values were obtained by minimizing the AAE for the range of saturated liquid given previously.

$$\begin{aligned} s_{\text{CO}_2} &= 1.585 \text{ cc/mole (from matching the saturated liquid density at } T_r = 0.712, \text{ CO}_2 \text{ triple point)} \\ s_{\text{H}_2\text{S}} &= 2.998 \text{ cc/mole (from matching the saturated liquid density at } T_r = 0.7097) \\ v_{c,\text{CO}_2} &= 96.001 \text{ cc/mole (2\% larger than the experimental critical volume)} \\ v_{c,\text{H}_2\text{S}} &= 100.490 \text{ cc/mole (2.5\% larger than the experimental critical volume)} \end{aligned}$$

For the PT equation, this study used the following parameters:

$$\begin{aligned} \text{CO}_2: & F = 0.707727 \quad \zeta_c = 03.09 \\ \text{H}_2\text{S}: & F = 0.583165 \quad \zeta_c = 03.20 \end{aligned}$$

These were taken from Patel and Teja¹³. The above values result in smaller errors in the density than the values from the generalized correlations.

Mixtures

Equation of the state models require binary interaction parameters for multicomponent input parameters. This study used binary interaction coefficients for H₂S – CO₂ as follows:

$$\begin{aligned} & 0.0989 \text{ for SRK} \\ & 0.0974 \text{ for PR} \\ & 0.0975 \text{ for PT} \end{aligned}$$

The values for the SRK and PR equations are from Knapp.¹⁹ These values are those given in the book by Reid.³ The interaction parameter for the PT equation is an estimate based on the values for the other two equations.

Equation-of-state summary

The following provides the details of the three equations of state used in this study.

Soave-Redlich-Kwong

$$P = \frac{R \cdot T}{v - b} - \frac{a}{v \cdot (v + b)}$$

$$Z^3 - Z^2 + (A - B - B^2) \cdot Z - (A \cdot B) = 0$$

where:

$$a_{ci} = 0.42748 \cdot \frac{(R \cdot T_{ci})^2}{P_{ci}}$$

$$a_i = a_{ci} \cdot \alpha_i$$

$$\alpha_i^{0.5} = 1 + m_i \cdot (1 - T_r^{0.5})$$

$$m_i = 0.48 + 1.574 \cdot \omega_i - 0.176 \cdot \omega_i^2$$

$$a = \sum_i^N \sum_j^N x_i x_j \cdot (a_i a_j)^{0.5} \cdot (1 - k_{ij})$$

$$A = \frac{a \cdot P}{(R \cdot T)^2}$$

$$b_i = 0.08664 \cdot \frac{R \cdot T_{ci}}{P_{ci}}$$

$$b = \sum_i^N x_i \cdot b_i$$

$$B = \frac{b \cdot P}{R \cdot T}$$

For unsaturated fluids in the subcritical region, only one of the roots, the most thermodynamically stable, is physically meaningful. For sub-critical saturated fluids, two roots of equal thermodynamic stability are physically meaningful.

It is worth noting that high temperature, single-phase fluids may also produce three real roots, one or more being negative. Neglected are negative roots, or specific volume roots less than the co-volume of the equation of state, b (see box).

After one calculates the molar vol-

ume, v , Equation 1 (see equation box) provides the molar density, $\tilde{\rho}$.

Furthermore, Equation 2 calculates the mass density, ρ , which is the normal definition of the density. In Equation 2, M is the molar mass (molecular weight) of the fluid.

Volume shifting

Volume shifting is a popular method for improving density predictions from cubic equations of state. In its simplest form, originally proposed by Peneloux,¹⁶ volume shifting is a correction to the calculated molar volume

(Equation 3). In Equation 3, v_{EoS} is the volume estimated from the equation of state and c is the volume-shift parameter, which in this case is a constant.

If one properly selects the volume shift parameter, then the corrected volume should be an improved estimate of the true molar volume. Peneloux suggested fitting the saturated liquid density at $T_r = 0.7$ to obtain the volume-shift parameter. Alternatively, one could use the volume-shift parameter as an adjustable parameter, which is fit by minimizing the error in the density prediction.

Peng-Robinson

$$P = \frac{R \cdot T}{v - b} - \frac{a}{v \cdot (v + b) + b \cdot (v - b)}$$

$$Z^3 - (1 - B) \cdot Z^2 + (A - 2 \cdot B - 3 \cdot B^2) \cdot Z - (A \cdot B - B^2 - B^3) = 0$$

where

$$a_{ci} = 0.457235 \cdot \frac{(R \cdot T_{ci})^2}{P_{ci}}$$

$$a_i = a_{ci} \cdot \alpha_i$$

$$\alpha_i^{0.5} = 1 + m_i \cdot (1 - T_r^{0.5})$$

$$m_i = 0.37464 + 1.54226 \cdot \dot{u}_i - 0.26992 \cdot \dot{u}_i^2$$

$$a = \sum_i^N \sum_j^N x_i x_j \cdot (a_i a_j)^{0.5} \cdot (1 - k_{ij})$$

$$A = \frac{a \cdot P}{(R \cdot T)^2}$$

$$b_i = 0.077796 \cdot \frac{R \cdot T_{ci}}{P_{ci}}$$

$$b = \sum_i^N x_i \cdot b_i$$

$$B = \frac{b \cdot P}{R \cdot T}$$

Patel-Teja

$$P = \frac{R \cdot T}{v - b} - \frac{a}{v \cdot (v + b) + c \cdot (v - b)}$$

$$Z^3 + (C - 1) \cdot Z^2 + (-2 \cdot B \cdot C - B^2 - B - C + A) \cdot Z + (B^2 \cdot C + B \cdot C - A \cdot B) = 0$$

where

$$a_{ci} = \Omega_a \cdot \frac{(R \cdot T_{ci})^2}{P_{ci}}$$

$$a_i = a_{ci} \cdot \alpha_i$$

$$\alpha_i^{0.5} = 1 + F \cdot (1 - T_r^{0.5})$$

$$a = \sum_i^N \sum_j^N x_i x_j \cdot (a_i a_j)^{0.5} \cdot (1 - k_{ij})$$

$$A = \frac{a \cdot P}{(R \cdot T)^2}$$

$$b_i = \Omega_b \cdot \frac{(R \cdot T_{ci})}{P_{ci}}$$

$$b = \sum_i^N x_i \cdot b_i$$

$$B = \frac{b \cdot P}{R \cdot T}$$

$$c_i = \Omega_c \cdot \frac{(R \cdot T_{ci})}{P_{ci}}$$

$$c = \sum_i^N x_i \cdot c_i$$

$$C = \frac{c \cdot P}{R \cdot T}$$

$$\Omega_a = 3 \cdot \zeta_c^2 + 3 \cdot (1 - 2 \cdot \zeta_c) \cdot \Omega_b + \Omega_b^2 - 3 \cdot \zeta_c^3$$

and Ω_b is the smallest real root of the following equation:

$$\Omega_b^3 + (2 - 3 \cdot \zeta_c) \cdot \Omega_b^2 + 3 \cdot \zeta_c^2 \cdot \Omega_b - \zeta_c^3 = 0$$

$$c = 1 - 3 \cdot \zeta_c$$

The parameters F and ζ_c can be optimized from a set of data or they can be obtained from the following generalized equations:

$$F = 0.4521413 + 1.30982 \cdot \omega - 0.295937 \cdot \omega^2$$

$$\zeta_c = 0.329032 - 0.076799 \cdot \omega - 0.0211947 \cdot \omega^2$$

To apply this method to mixtures, one assumes that the c for the mixture, c_{mix} , is the mole-fraction weighted average of the parameters for the pure components (Equation 4). In this equation, x_i , is the mole fraction of component i , and c_i is the volume shift parameter for component i .

Mathias¹⁷ noted that the volume-shift method of Peneloux improved the liquid density prediction only up to a reduced temperature of about 0.85. To improve the prediction over the entire range Mathias proposed an extended correction procedure that begins with

Equation 5. In Equation 5 the s is a volume-shift parameter and it is a constant, and δ , the bulk modulus, is a dimensionless parameter which is defined by Equation 6.

In Equation 6, R is the universal gas constant, T is absolute temperature, and P is total pressure. This expression can be evaluated from the equation of state.

Finally the function, f_c , was chosen such that the volume shifting procedure calculated the true critical point. For the PR equation, Equation 7 calculates this function, in which b is the co-volume from the equation of state.

For mixtures Mathias used the usual, simple mixing rule provided by Equation 8.

Others have proposed making the volume-shift parameter with different functions of temperature. This adds to the model complexity. In addition, a poorly constructed temperature-dependence can lead to thermodynamic consistency problems; for example, see Monnery.¹⁸

This study only examines the corrections proposed by Peneloux and Mathias. Values of c and s for CO_2 and H_2S used in this study are listed in the box.

CO₂ DENSITY ERROR EVALUATION

Table 2

| Region | AE, % | AAE, % | MaxE, % |
|------------------------------|-------|--------|---------|
| Original SRK equation | | | |
| Liquid region | 13.38 | 13.38 | 15.76 |
| Vapor region | 0.49 | 0.49 | 2.25 |
| Near critical region | 13.26 | 13.26 | 24.68 |
| Supercritical region | 6.31 | 6.31 | 14.30 |
| Saturated liquid | 15.25 | 15.25 | 17.11 |
| Saturated vapor | 2.64 | 2.64 | 3.15 |
| Overall | 5.41 | 5.41 | 24.68 |
| SRK-Peneloux equation | | | |
| Liquid region | -2.44 | 2.83 | 5.76 |
| Vapor region | -0.66 | 0.66 | 1.87 |
| Near critical region | 4.43 | 5.34 | 17.33 |
| Supercritical region | -1.79 | 2.49 | 13.47 |
| Saturated liquid | 0.79 | 2.05 | 4.26 |
| Saturated vapor | 0.16 | 0.16 | 0.25 |
| Overall | -0.90 | 2.41 | 17.33 |
| Original PR equation | | | |
| Liquid region | 2.20 | 2.20 | 4.92 |
| Vapor region | -1.09 | 1.09 | 2.81 |
| Near critical region | 5.52 | 6.51 | 16.66 |
| Supercritical region | 0.40 | 2.11 | 7.05 |
| Saturated liquid | 4.17 | 4.17 | 6.52 |
| Saturated vapor | -0.84 | 0.84 | 1.05 |
| Overall | 0.45 | 2.25 | 16.66 |
| PR-Peneloux equation | | | |
| Liquid region | -1.37 | 1.81 | 3.65 |
| Vapor region | -1.33 | 1.33 | 3.50 |
| Near critical region | 3.55 | 5.23 | 14.97 |
| Supercritical region | -1.34 | 2.32 | 8.18 |
| Saturated liquid | 0.87 | 1.62 | 3.57 |
| Saturated vapor | -1.36 | 1.36 | 1.70 |
| Overall | -0.93 | 2.39 | 14.97 |
| PR-Mathias equation | | | |
| Liquid region | -0.37 | 0.49 | 0.99 |
| Vapor region | -1.46 | 1.46 | 4.85 |
| Near critical region | -0.33 | 3.93 | 7.54 |
| Supercritical region | -1.24 | 1.78 | 5.49 |
| Saturated liquid | 0.20 | 0.42 | 0.94 |
| Saturated vapor | -2.22 | 2.22 | 3.01 |
| Overall | -1.21 | 1.83 | 7.54 |
| Original PT equation | | | |
| Liquid region | 3.06 | 3.06 | 5.77 |
| Vapor region | -1.00 | 1.00 | 2.56 |
| Near critical region | 6.07 | 6.92 | 17.32 |
| Supercritical region | 0.69 | 2.12 | 7.39 |
| Saturated liquid | 5.04 | 5.04 | 7.36 |
| Saturated vapor | -0.54 | 0.54 | 0.69 |
| Overall | 0.75 | 2.30 | 17.32 |

H₂S DENSITY ERROR EVALUATION

Table 3

| Region | AE, % | AAE, % | MaxE, % |
|------------------------------|-------|--------|---------|
| Original SRK equation | | | |
| Liquid region | 7.29 | 7.29 | 14.05 |
| Vapor region | -0.29 | 0.59 | 1.87 |
| Near critical region | 10.26 | 10.45 | 21.34 |
| Supercritical region | 6.66 | 7.14 | 12.66 |
| Saturated liquid | 8.86 | 8.86 | 14.15 |
| Saturated vapor | 1.23 | 1.23 | 1.76 |
| Overall | 4.08 | 4.49 | 21.34 |
| SRK-Peneloux equation | | | |
| Liquid region | 0.33 | 2.66 | 9.28 |
| Vapor region | -0.74 | 0.90 | 3.10 |
| Near critical region | 7.26 | 8.09 | 18.29 |
| Supercritical region | 2.86 | 4.00 | 9.09 |
| Saturated liquid | 2.40 | 3.58 | 9.40 |
| Saturated vapor | 0.65 | 0.92 | 1.48 |
| Overall | 0.66 | 2.56 | 18.29 |
| Original PR equation | | | |
| Liquid region | -4.88 | 5.17 | 7.91 |
| Vapor region | -1.92 | 1.94 | 6.37 |
| Near critical region | 3.08 | 6.26 | 12.74 |
| Supercritical region | -0.86 | 3.16 | 6.08 |
| Saturated liquid | -3.23 | 4.08 | 7.73 |
| Saturated vapor | -0.89 | 1.40 | 3.79 |
| Overall | -2.47 | 3.58 | 12.74 |
| PR-Peneloux equation | | | |
| Liquid region | 0.28 | 1.70 | 6.74 |
| Vapor region | -1.61 | 1.65 | 5.36 |
| Near critical region | 5.27 | 7.56 | 15.05 |
| Supercritical region | 1.88 | 3.91 | 7.91 |
| Saturated liquid | 1.59 | 2.39 | 6.84 |
| Saturated vapor | -0.49 | 1.18 | 2.99 |
| Overall | -0.03 | 2.41 | 15.05 |
| PR-Mathias equation | | | |
| Liquid region | -0.76 | 1.02 | 1.79 |
| Vapor region | -2.03 | 2.06 | 7.60 |
| Near critical region | -0.11 | 4.53 | 7.69 |
| Supercritical region | -0.69 | 2.38 | 6.86 |
| Saturated liquid | -0.27 | 0.92 | 1.84 |
| Saturated vapor | -1.14 | 1.64 | 4.70 |
| Overall | -1.25 | 1.94 | 7.69 |
| Original PT equation | | | |
| Liquid region | 1.19 | 2.03 | 8.53 |
| Vapor region | -1.10 | 1.18 | 3.94 |
| Near critical region | 6.77 | 8.03 | 16.94 |
| Supercritical region | 3.08 | 4.48 | 9.25 |
| Saturated liquid | 2.78 | 3.15 | 8.64 |
| Saturated vapor | 0.07 | 0.96 | 1.85 |
| Overall | 0.83 | 2.45 | 16.94 |

tematic deviation between the function (values) and the predictions (estimates).

Finally, Equation 13 determines the maximum error, MaxE. The maximum error gives the largest deviation of the model from the data values.

There are other methods for estimating the error of a model, but the ones discussed are sufficient for the purposes of this study.

Pure components

Table 1 lists the six regions for which the study evaluated the errors for the various density prediction methods.

Tables 2 and 3 list the errors predicted for the density of pure CO₂ and H₂S, while Figs. 1 and 2 display a portion of the error data for each equation over the various regions.

These tables and figures show that the density predictions from the SRK equation are unsatisfactory. Although the overall average error is only about 5%, the maximum

errors often exceed 15% and not only in the near critical region.

The PR equation is better at predicting the densities of these components than is the SRK equation, which is as expected. For H₂S, the PT equation is a further improvement over the PR equation, again as expected.

For CO₂, however, the PT equation does not improve the density predictions over the PR equation. As a check that the implementation of the PT was correct, the study set c to 0.3074, which reduces the PT equation to the PR equation. The calculated results obtained for this form of the PT equation were identical to those from the PR equation.

In all cases, the volume-shifting results in an improvement in the predict-

Error estimation

The study examined six density calculation methods, as follows:

1. The original SRK.
2. The SRK with a Peneloux-type volume shift.
3. The original Peng-Robinson equation.
4. The PR equation with a Peneloux-type volume shift.
5. The PR equation with a Mathias-type volume shift'
6. The PT equation.

The box presents a complete list of parameters used in this study.

Equation 9 defines the error for a given point, as a percentage. In this equation, tabular data provide the "value" and an equation, calculated at the same conditions, derives the "estimate."

Equation 10 defines the absolute error and Equation 11 defines the average error, AE, expressed as a percentage. The NP is the number of points.

The average error can be a positive or negative value. The better fit, however, occurs when the average error is close to zero.

Equation 12 defines the absolute average error. The difference between the AE and the AAE is that positive and negative errors in AE tend to cancel each other, making the prediction look better than it may actually be.

The average absolute error can only have a positive value because of the absolute value function. It is a better indication of the "goodness of fit" than is the average error. A small AE and a relatively large AAE usually indicates a sys-

EQUATIONS

$$\tilde{\rho} = \frac{1}{v}$$

$$\rho = \frac{M}{v}$$

$$v_{\text{corrected}} = v_{\text{EoS}} + C$$

$$C_{\text{mix}} = \sum_{i=1}^{NC} x_i c_i$$

$$v_{\text{corrected}} = v_{\text{EoS}} + s + f_c \left(\frac{0.41}{0.41 + \delta} \right)$$

$$\delta = -\frac{v^2}{RT} \left(\frac{\partial P}{\partial v} \right)_T$$

$$f_c = v_c - (3.946b + s)$$

$$(1) \quad s_{\text{mix}} = \sum_{i=1}^{NC} x_i s_i \quad (8)$$

$$(2) \quad \text{Error} = \frac{\text{value}(i) - \text{estimate}(i)}{\text{value}(i)} \times 100\% \quad (9)$$

$$(3) \quad \text{Abs. Error} = \frac{|\text{value}(i) - \text{estimate}(i)|}{\text{value}(i)} \times 100\% \quad (10)$$

$$(4) \quad \text{AE} = \frac{1}{NP} \sum_{i=1}^{NP} \frac{\text{value}(i) - \text{estimate}(i)}{\text{value}(i)} \times 100\% \quad (11)$$

$$(5) \quad \text{AAE} = \frac{1}{NP} \sum_{i=1}^{NP} \frac{|\text{value}(i) - \text{estimate}(i)|}{\text{value}(i)} \times 100\% \quad (12)$$

$$(6) \quad \text{MaxE} = \text{maximum} \left[\frac{|\text{value}(i) - \text{estimate}(i)|}{\text{value}(i)} \times 100\%, i = 1, 2, \dots, NP \right] \quad (13)$$

(7)

ed liquid density. Overall, however, volume shifting does not always result in an improvement. For example, for CO₂, the density predictions with the Peneloux-type volume shift of the PR equation actually are worse than the original PR equation. The reason for this is that the volume shifting results in worse predictions of the vapor density.

Mixtures

Table 4 shows the errors for predicting the data from Robinson.⁸ Because these data are only for the vapor phase they were not divided into regions for analysis. In general, the errors for these mixtures are relatively small although a few points have larger errors.

The data set of Kellerman¹⁰ is sufficiently large that it was examined in three regions, and Table 5 gives the definitions of these three regions and summarizes the errors for the six equations.

Figs. 3 presents plots of the errors for the predictions from the six equations for the various mixtures.

In general the observations for the pure components hold true for the binary mixture data. For example, the SRK equation predict unsatisfactory the density values.

The PR equation predicts the mixture data with acceptable accuracy, with the maximum error being less than

10%.

Although the volume-shift methods improve the predictions for the liquid density, the overall density predictions are only marginally improved.

Finally, the PT equation is an improvement over the PR equation when one considers the overall errors. The maximum error for the PT equation, however,

components. Overall, the average error for both the pure components is less than 5% and for the mixtures, less than 10%. Only in the near critical region do errors exceed 10%.

Volume-shifting the PR equations tends to improve density predictions in the liquid region. The predictions from the Peneloux-type volume shift have an overall error of 2.5%, and the errors from the Mathias-type are less than 2%.

The PT equation, although somewhat more complex, does not significantly improve the density calculations.

The observations for pure components are basically the same as for the mixtures examined. The SRK is unsatisfactory for predicting the density of these mixtures. The other five equations of state and modifications are all sufficiently accurate for engineering calculations, except in the region near a critical point. ♦

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VAPOR PHASE MIXTURE DENSITY ERRORS* Table 4

| Equation | AE, % | AAE, % | MaxE, % |
|--------------|-------|--------|---------|
| SRK | 1.96 | 2.47 | 14.01 |
| SRK-Peneloux | 0.43 | 1.46 | 9.23 |
| PR | -0.21 | 1.51 | 10.86 |
| PR-Peneloux | -0.34 | 1.49 | 10.44 |
| PR-Mathias | -0.87 | 1.64 | 13.67 |
| PT | 0.01 | 1.45 | 10.11 |

*Data set from Robinson.⁹

is about equal to that for the PR.

Study results

The study concludes that the original SRK equation is not sufficiently accurate for predicting the density of acid gas. Although the average errors are acceptable, the maximum errors in the various regions exceed 10%.

The Peneloux-type volume shifting improves this equation significantly. For the pure components, only in the near-critical region do errors exceed 10%. For the mixture data, the maximum errors are typically less than 11%.

The original PR equation is accurate for predicting the densities of pure

MIXTURE DENSITY ERRORS

Table 5

| | Reduced temperature | Reduced pressure | |
|------------------------------|-------------------------|--|---------|
| 1. Liquid region | $T_r < 1.0$ | $P_r > P_r(\text{bubble})$ | |
| 2. Vapor region | $T_r > T_r(\text{dew})$ | $P_r < P_r(\text{dew})$ or $P_r < 1.0$ | |
| 3. Supercritical region | $T_r > 1.0$ | $P_r > 1.0$ | |
| Region | AE, % | AAE, % | MaxE, % |
| Original SRK equation | | | |
| Liquid region | 9.23 | 9.23 | 18.87 |
| Vapor region | 0.51 | 0.51 | 4.51 |
| Supercritical region | 2.75 | 2.79 | 6.88 |
| Overall | 3.54 | 3.55 | 18.87 |
| SRK-Peneloux equation | | | |
| Liquid region | -4.31 | 5.00 | 10.35 |
| Vapor region | -0.64 | 0.65 | 1.86 |
| Supercritical region | -2.87 | 2.89 | 10.73 |
| Overall | -2.46 | 2.64 | 10.73 |
| Original PR equation | | | |
| Liquid region | -1.34 | 2.81 | 9.94 |
| Vapor region | -1.26 | 1.26 | 2.99 |
| Supercritical region | -2.62 | 2.76 | 8.47 |
| Overall | -1.86 | 2.27 | 9.94 |
| PR-Peneloux equation | | | |
| Liquid region | -2.84 | 3.53 | 7.88 |
| Vapor region | -1.39 | 1.39 | 3.22 |
| Supercritical region | -3.23 | 3.24 | 9.41 |
| Overall | -2.52 | 2.68 | 9.41 |
| PR-Mathias equation | | | |
| Liquid region | -2.64 | 2.71 | 5.79 |
| Vapor region | -1.64 | 1.64 | 4.88 |
| Supercritical region | -4.90 | 4.90 | 11.83 |
| Overall | -3.26 | 3.28 | 11.83 |
| Original PT equation | | | |
| Liquid region | 0.39 | 2.16 | 10.56 |
| Vapor region | -1.02 | 1.02 | 2.48 |
| Supercritical region | -2.02 | 2.26 | 7.23 |
| Overall | -1.11 | 1.82 | 10.56 |

Note: Data set from Kellerman.¹⁰

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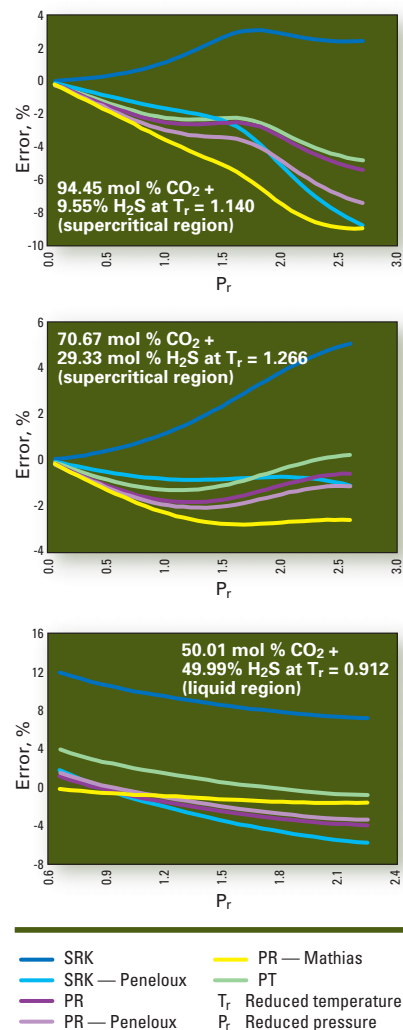
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MIXTURE DENSITY ERRORS

Fig. 3



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