Sour Natural Gas and Liquid Equation of State

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Abstract

The major gaseous impurities in the subquality natural gas sources are acidic components, such as hydrogen sulfide and carbon dioxide. Considering that H$_2$S easily dissociates into hydrogen and elemental sulfur, thermodynamic properties and specially phase equilibria of liquid and gaseous systems containing hydrogen, hydrogen sulfide, carbon dioxide, other acidic components, and light hydrocarbons are of much interest to the natural gas and gas condensate production industries.

In this paper we report the development of a simple and accurate cubic equation of state for prediction of thermodynamic properties and phase behavior of sour natural gas and liquid mixtures. This cubic equation of state, which is based on statistical mechanical theoretical grounds, is applied to pure fluids as well as mixtures with quite accurate results. All the thermodynamic property relations of sour gaseous and liquid mixtures are derived and reported in this report. Parameters of this equation of state are derived for different components of sour natural gas systems. The resulting equation of state is tested for phase behavior and other thermodynamic properties of simulated and natural sour gas mixtures. It is shown that the proposed equation of state is simple and predicts the properties of interest with ease and accuracy.

1. Introduction

In the past two decades, a number of subquality natural gas/gas condensate fields have been discovered around the world, Campbell (1976). The major impurities of these subquality natural gas/gas condensate sources consist of N$_2$, CO$_2$ and H$_2$S. Because H$_2$S easily dissociates into hydrogen and elemental sulfur, thermodynamic properties and specially phase equilibria of liquid and gaseous systems containing hydrogen, hydrogen sulfide, carbon dioxide, other acidic components, and light hydrocarbons are of much interest to the natural gas and gas condensate production industries (Campbell, 1976; Katz and Lee, 1990; Mansoori and Savidge, 1989).

Transportation, and processing of sour and hydrogen-containing natural gas is of major concern to the industries involved. Carbon dioxide and hydrogen sulfide are considered as being impurities in natural gas and oil and are responsible for corrosion of the flowline and processing equipment. Separation of these gases from natural gas and oil is usually the most expensive part of natural gas and oil treatment processes. The economical importance of treatment of sour gas has made it important for the gas and oil industry to have accurate equation of state to represent properties of sour gases and liquid mixtures (Katz and Lee, 1990; Edmister and Lee, 1986). Presence of sour gases in crude oil could also cause deposition of heavy organics, such as asphaltene and wax, from oil which would plug the well, pipeline and refining equipment (Mansoori and Jiang, 1985).
As of yet no satisfactory equation of state has been available to predict the behavior of sour gases and liquids in reservoir, well, pipeline and compression/expansion facilities (Wichert and Aziz, 1972). Recently, experimental and modeling studies on the phase behavior of high H$_2$S-content natural gas mixtures were reported by Gu et al. (1993). These workers used the Peng-Robinson (PR) equation of state for phase equilibria calculations, but because the PR equation was not accurate for PVT calculation, they used instead a 33-constant super equation of state. By using this equation of state, Li and Guo (1991) studied the supercompressibility and compressibility factors of natural gas mixtures. However, it is not convenient for engineering calculations to use such a complex equation. Morris and Byers (1991) have performed some experimental work to obtain VLE data for binary and ternary systems containing CH$_4$, CO$_2$ and H$_2$S. Afterwards, they used the PR and Soave-Redlich-Kwong (SRK) equations of state for VLE calculations of the same systems and compared their experimental results with these calculations. In 1978, Huron et al. (1978) and in 1979, Evelein and Moore (1979) used the SRK equation of state to study the hydrocarbon systems containing hydrogen sulfide or carbon dioxide. They reported phase equilibria calculations, but did not report other thermodynamic property calculations. On the same subject, some other experimental research works have been reported, such as the works of Morris and Byers (1990), Huang et al. (1985), Robinson et al. (1978), Mraw et al. (1978) and Eakin and Devaney (1975). By reviewing the above literature on equations of state sour gases and liquids, it is concluded that there is no simple and accurate equation of state available for predicting thermodynamic properties of sour and hydrogen-containing gases and liquids.

In this paper we report the development of an accurate equation of state for sour and hydrogen-containing natural gas/gas condensate systems. This equation of state is tested with success for a variety of cases of interest in natural gas engineering for which experimental data are available for comparison. The basic aim of the present paper is to produce a simple two-constant cubic equation of state which is capable of calculating thermodynamic properties and phase behavior of sour natural gases and liquids. This equation of state is designed specially to predict thermodynamic properties and phase equilibria of liquids and vapors which consist of hydrogen, methane, other light hydrocarbons and acidic components appearing in the natural gas and gas condensate streams.

In the first part of this report we introduce a two-constant cubic equation of state. This cubic equation of state, which is based on statistical mechanical theoretical grounds, is extended to mixtures. Then parameters of this equation of state are derived for different components of sour natural gas systems. The resulting equation of state is tested for phase behavior and other thermodynamic properties of simulated and natural sour gas mixtures. It is shown that the present equation of state, even though it is simple, predicts the properties of interest with ease and accuracy.

2. The equation of state

A new simple two-constant cubic equation of state for hydrocarbons, hydrocarbon mixtures, and other non-associating fluids was introduced earlier by Mohsen-Nia et al. (1993). This equation of state model is based on the statistical mechanical information available for the repulsive thermodynamic functions and the phenomenological knowledge of the attractive potential tail contributions to the thermodynamic properties. This new two-constant-parameter cubic equation is in the following form:

\[ Z = (v + 1.3191b) / ((v - b) - a / [RT^{3/2}(v + b)]) \tag{1} \]

Eq. 1 is cubic in terms of volume and contains only two adjustable parameters. By applying the critical point constraints on the above equation, parameters $a$ and $b$ are determined to be (Mohsen-Nia et al., 1993):

\[ a = 0.486989R^2T_c^{5/2}/P_c \]
\[ b = 0.064662RT_c/P_c \tag{2} \]

The critical compressibility factor based on this equation of state is calculated to be:

\[ Z_c = 1/3 \tag{3} \]

the same as the Redlich-Kwong (RK) equation of state. It is shown that this equation of state is more accurate than the Redlich-Kwong equation, which had been considered to be the best two-constant-parameter cubic equation of state (Mohsen-Nia et al., 1993). For mul-
Table 1
Equation of state constants

<table>
<thead>
<tr>
<th>Substances</th>
<th>$\alpha_i$</th>
<th>$\beta_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major components of sour natural gas</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$</td>
<td>-0.07099</td>
<td>0.12307</td>
</tr>
<tr>
<td>N$_2$</td>
<td>-0.02474</td>
<td>0.06393</td>
</tr>
<tr>
<td>CO</td>
<td>-0.02281</td>
<td>0.06066</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>-0.00580</td>
<td>0.01456</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>-0.02351</td>
<td>0.04207</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>-0.03662</td>
<td>0.05957</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>-0.02898</td>
<td>0.03865</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>-0.02133</td>
<td>0.04504</td>
</tr>
<tr>
<td>C$_3$H$_6$</td>
<td>-0.00841</td>
<td>0.04624</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>-0.01457</td>
<td>0.03657</td>
</tr>
<tr>
<td>Components of natural gas in minute quantities</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-C$<em>4$H$</em>{10}$</td>
<td>-0.00663</td>
<td>0.03613</td>
</tr>
<tr>
<td>i-C$<em>4$H$</em>{10}$</td>
<td>-0.01373</td>
<td>0.02852</td>
</tr>
<tr>
<td>n-C$<em>5$H$</em>{12}$</td>
<td>-0.00878</td>
<td>0.02251</td>
</tr>
<tr>
<td>n-C$<em>6$H$</em>{14}$</td>
<td>-0.00761</td>
<td>0.01258</td>
</tr>
<tr>
<td>n-CH$_{16}$</td>
<td>0.00425</td>
<td></td>
</tr>
</tbody>
</table>

ticompont mixtures this equation of state assumes the following form (Mohsen-Nia et al., 1993):

$$Z_m = \frac{(v + 1.3191b_{Rm})}{(v - b_{Rm})} - \sum_j x_j a_{ij} / \left[ RT^{3/2} (v + \sum_j x_j b_{ij}) \right]$$  \hspace{1cm} (4)

where $b_{Rm}$ is defined as:

$$b_{Rm} = (3/4) \sum_j x_j b_{ij} + (1/4) \sum_j x_j b_{ij}$$  \hspace{1cm} (5)

Table 2
Comparison of the proposed, PR and SRK equations of state for density ($\rho$), enthalpy ($H$) and entropy ($S$) predictions of the major pure components of sour natural gas

<table>
<thead>
<tr>
<th>Substance</th>
<th>T (K)</th>
<th>P (bar)</th>
<th>No. of data points</th>
<th>SRK $\rho$ (%)</th>
<th>SRK $H$ (%)</th>
<th>SRK $S$ (%)</th>
<th>PR $\rho$ (%)</th>
<th>PR $H$ (%)</th>
<th>PR $S$ (%)</th>
<th>Proposed $\rho$ (%)</th>
<th>Proposed $H$ (%)</th>
<th>Proposed $S$ (%)</th>
<th>AAD %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>110-500</td>
<td>10-500</td>
<td>90</td>
<td>2.4</td>
<td>1.9</td>
<td>0.5</td>
<td>5.3</td>
<td>1.0</td>
<td>0.9</td>
<td>1.8</td>
<td>1.2</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>200-500</td>
<td>1.5-350</td>
<td>80</td>
<td>3.1</td>
<td>1.0</td>
<td>0.5</td>
<td>5.1</td>
<td>0.6</td>
<td>1.3</td>
<td>2.2</td>
<td>1.0</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Ethylene</td>
<td>150-450</td>
<td>10-400</td>
<td>70</td>
<td>3.7</td>
<td>2.6</td>
<td>0.8</td>
<td>4.7</td>
<td>0.8</td>
<td>1.1</td>
<td>1.7</td>
<td>1.1</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>150-560</td>
<td>0.5-500</td>
<td>80</td>
<td>4.5</td>
<td>0.8</td>
<td>0.5</td>
<td>4.6</td>
<td>2.5</td>
<td>0.4</td>
<td>2.5</td>
<td>3.1</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Propylene</td>
<td>100-600</td>
<td>10-400</td>
<td>75</td>
<td>4.0</td>
<td>2.6</td>
<td>2.5</td>
<td>5.0</td>
<td>1.6</td>
<td>2.3</td>
<td>1.6</td>
<td>1.9</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>20-500</td>
<td>0.1-400</td>
<td>70</td>
<td>1.3</td>
<td>0.5</td>
<td>2.4</td>
<td>6.0</td>
<td>2.1</td>
<td>1.7</td>
<td>2.3</td>
<td>0.8</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>74-700</td>
<td>0.75-500</td>
<td>60</td>
<td>2.9</td>
<td>0.8</td>
<td>0.7</td>
<td>4.7</td>
<td>0.8</td>
<td>0.5</td>
<td>2.2</td>
<td>0.8</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>80-600</td>
<td>5.0-500</td>
<td>85</td>
<td>1.4</td>
<td>0.5</td>
<td>0.7</td>
<td>5.3</td>
<td>0.6</td>
<td>0.3</td>
<td>1.4</td>
<td>0.5</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>250-1000</td>
<td>2.0-500</td>
<td>90</td>
<td>8.0</td>
<td>0.5</td>
<td>1.7</td>
<td>1.8</td>
<td>0.4</td>
<td>0.5</td>
<td>2.1</td>
<td>0.4</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>H$_2$S</td>
<td>255-480</td>
<td>1.0-210</td>
<td>80</td>
<td>2.6</td>
<td>2.4</td>
<td>0.2</td>
<td>4.4</td>
<td>3.1</td>
<td>0.4</td>
<td>1.5</td>
<td>1.7</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>AAD %</td>
<td>3.4</td>
<td>1.3</td>
<td>1.1</td>
<td>4.7</td>
<td>1.4</td>
<td>0.9</td>
<td>1.9</td>
<td>1.2</td>
<td>0.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Edmister and Lee, 1986; Hall et al., 1983; Chorn and Mansoori, 1988). For this purpose we replace parameters $a$ and $b$ with the following temperature-dependent expressions:

$$a = a_c \alpha(T_r) \quad \text{and} \quad b = b_c \beta(T_r) \quad (8)$$

where:

$$a_c = 0.486989 R^2 T_r^{-12} / P_c \quad \text{and} \quad (9)$$

$$b_c = 0.064662 R T_r / P_c \quad (9)$$

The dimensionless temperature-dependent parameters $\alpha(T_r)$ and $\beta(T_r)$, while being different, reduce to unity at the critical point:

$$\alpha(T_r = 1) = \beta(T_r = 1) = 1 \quad (10)$$

There have been a variety of empirical functional forms for $\alpha$ and $\beta$ reported in the literature. However, in line with the variational and perturbation molecular theories of fluids (Mansoori and Canfield, 1970), we may use the following polynomial expression for $\beta(T_r)$:

$$\beta(T_r)^{1/3} = \frac{1 + \beta_1 / T_r + \beta_2 / T_r^2 + \ldots}{1 + \beta_1 / 1 + \beta_2 + \ldots} \quad (11)$$

Table 3

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$P$ (bar)</th>
<th>$Z_{exp}$</th>
<th>SRK</th>
<th>PR</th>
<th>Proposed</th>
</tr>
</thead>
<tbody>
<tr>
<td>300.10</td>
<td>318.29</td>
<td>0.8870</td>
<td>0.9311</td>
<td>0.8629</td>
<td>0.9146</td>
</tr>
<tr>
<td>320.06</td>
<td>372.49</td>
<td>0.9736</td>
<td>1.0169</td>
<td>0.9439</td>
<td>0.9997</td>
</tr>
<tr>
<td>288.79</td>
<td>287.52</td>
<td>0.8326</td>
<td>0.8763</td>
<td>0.8113</td>
<td>0.8603</td>
</tr>
<tr>
<td>273.19</td>
<td>245.07</td>
<td>0.7500</td>
<td>0.7923</td>
<td>0.7322</td>
<td>0.7769</td>
</tr>
<tr>
<td>260.02</td>
<td>209.51</td>
<td>0.6736</td>
<td>0.7127</td>
<td>0.6574</td>
<td>0.6978</td>
</tr>
<tr>
<td>250.06</td>
<td>183.18</td>
<td>0.6123</td>
<td>0.6467</td>
<td>0.5955</td>
<td>0.6321</td>
</tr>
<tr>
<td>242.95</td>
<td>165.10</td>
<td>0.5680</td>
<td>0.5967</td>
<td>0.5484</td>
<td>0.5821</td>
</tr>
<tr>
<td>241.99</td>
<td>162.69</td>
<td>0.5620</td>
<td>0.5897</td>
<td>0.5418</td>
<td>0.5751</td>
</tr>
<tr>
<td>241.03</td>
<td>160.45</td>
<td>0.5564</td>
<td>0.5828</td>
<td>0.5353</td>
<td>0.5682</td>
</tr>
<tr>
<td>240.00</td>
<td>157.98</td>
<td>0.5502</td>
<td>0.5753</td>
<td>0.5282</td>
<td>0.5607</td>
</tr>
<tr>
<td>239.82</td>
<td>157.57</td>
<td>0.5492</td>
<td>0.5740</td>
<td>0.5270</td>
<td>0.5594</td>
</tr>
</tbody>
</table>

Overall % deviations

| 5.1 | 3.2 | 2.7 |
Table 4
Compositions (in mole fractions) of three different samples of sour natural gas used in the calculations reported in Table 5

<table>
<thead>
<tr>
<th>Components</th>
<th>Sample A</th>
<th>Sample B</th>
<th>Sample C</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>0.0000</td>
<td>0.0052</td>
<td>0.0081</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.7130</td>
<td>0.7458</td>
<td>0.8303</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.0000</td>
<td>0.2016</td>
<td>0.0744</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.0900</td>
<td>0.0474</td>
<td>0.0130</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.1970</td>
<td>0.0000</td>
<td>0.0735</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0007</td>
</tr>
</tbody>
</table>

Table 5
Comparison between the experimental (Katz and Lee, 1990; Buxton and Campbell, 1967; Satter and Campbell, 1963) and calculated compressibility factors for the three sour natural gas samples of Table 4 using the proposed, PR and SRK equations of state all with \(k_{ij}^s = 0\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>(T) (K)</th>
<th>(P) (bar)</th>
<th>Compressibility Factor (Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Exp.</td>
<td>SRK</td>
</tr>
<tr>
<td>A</td>
<td>311.93</td>
<td>70.72</td>
<td>0.830</td>
</tr>
<tr>
<td>A</td>
<td>337.87</td>
<td>70.72</td>
<td>0.856</td>
</tr>
<tr>
<td>A</td>
<td>311.93</td>
<td>139.65</td>
<td>0.714</td>
</tr>
<tr>
<td>A</td>
<td>337.87</td>
<td>139.65</td>
<td>0.762</td>
</tr>
<tr>
<td>B</td>
<td>310.93</td>
<td>70.72</td>
<td>0.865</td>
</tr>
<tr>
<td>B</td>
<td>310.93</td>
<td>139.65</td>
<td>0.778</td>
</tr>
<tr>
<td>B</td>
<td>310.93</td>
<td>208.58</td>
<td>0.778</td>
</tr>
<tr>
<td>C</td>
<td>310.93</td>
<td>112.0</td>
<td>0.821</td>
</tr>
</tbody>
</table>

Then for simplicity, and as a first approximation, we use the following form for \(\beta(T_r)\):

\[
\beta(T_r) = \left(1 + \beta_1/T_r\right)^3/(1 + \beta_1)^3
\]  
(12)

where \(\beta_1\) is a constant. Eq. 12 satisfies the basic theoretical conditions for \(\beta(T_r)\) at the critical point, i.e.,

\[
\beta(T_r) \rightarrow 1 \text{ at } T_r \rightarrow 1.
\]

This functional form will remain finite and positive for all possible temperature ranges. For symmetry and simplicity we also use the same functional form for parameter \(\alpha(T_r)\), i.e.:

\[
\alpha(T_r) = \left(1 + \alpha_1/T_r\right)^3/(1 + \alpha_1)^3
\]  
(13)

where \(\alpha_1\) is a constant. Eq. 13 also satisfies the basic theoretical conditions for \(\alpha(T_r)\) at the critical point, i.e., \(\alpha(T_r) \rightarrow 1 \text{ at } T_r \rightarrow 1\). It can also be inferred from the equation of state, that as the temperature tends to infinity, the attractive term of the equation of state, \(-a/\left[RT^{3/2}(v+b)\right]\), must approach to zero. The form of \(\alpha(T_r)\) considered in this work is conducive to this requirement.

The constants \(\alpha_1\) and \(\beta_1\) have been determined for the components of the sour natural gas and gas-condensate mixtures as reported in Table 1. These constants were found by minimization of vapor pressures and saturation liquid densities.

For ease of calculations, we have correlated parameters \(\alpha_1\) and \(\beta_1\) of the major components of natural gas (see Table 1) to their acentric factor in the following forms:

\[
\alpha_1 = -0.036139 + 0.14167w
\]

\[
\beta_1 = 0.0634 - 0.18769w
\]  
(14)

These correlations are for \(w\) in the range of \(-0.22 \leq w \leq 0.18\) and they do not hold very well for parameters of the components of natural gas which are in minute quantities (C₄ to C₇+). Because of the very small concentrations of these components in natural gas.
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in the computation of the natural gas thermodynamic properties. Formulation of equation of state of hydrocarbon mixtures containing appreciable amounts of heavier hydrocarbons requires the application of the continuous thermodynamics and Cγ+ fraction characterization techniques (Mansoori and Savidge, 1989; Chorn and Mansoori, 1988; Du and Mansoori, 1986, 1988), which is outside the scope of the present report.

One of the requirements of equations of state for industrial applications is their analytic representation of thermodynamic functions. Such properties of fluids (like entropy, enthalpy and fugacity) are of direct interest in energy balance and phase behavior calculations in industrial practice. The analytic expressions of these functions are as the following:

\[ \frac{H_m - H_{mig}}{RT} = (Z_m - 1) - 2.3191 T b_{Am} / (u - b_{Am}) \]
\[ - a_m' \ln [u / (u + b_{Am})] / R b_{Am} T^{1/2} \]
\[ + \left( \frac{b_{Am}'}{RT^{1/2}} \right) \left[ (a_m / b_{Am}) \ln [u / (u + b_{Am})] \right] \]
\[ + a_m / (b_{Am} (v + b_{Am})) \]
\[ + (1.5 a_m / b_{Am} R T^{3/2}) \ln [u / (u + b_{Am})] \] (15)

\[ S_m - S_{mig} / R = \ln Z_m + 2.3191 \ln [ (u - b_{Rm}) / u ] \]
\[ - 2.3191 T b_{Rm} / (u - b_{Rm}) \]
\[ - \frac{a'_{m}}{(b_{Am} T^{1/2})} \ln [u / (u + b_{Am})] \]
\[ + \left[ a_m b_{Am}' / T^{1/2} \right] \left[ (1 / b_{Am}) \ln [u / (u + b_{Am})] \right] \]
\[ + 1 / (b_{Am} v + b_{Am}^2) \]
\[ + \left[ a_m / (2 b_{Am} T^{3/2}) \right] \ln [u / (u + b_{Am})] \] (16)

\[ \ln f_i = -2.31915 \ln \left( 1 - b_{Rm} / u \right) \]
\[ + 2.3191 [d(n b_{Rm}) / d n_i] / (u - b_{Rm}) \]
\[ + [d(n b_{Am}) / d n_i] [a / (b_{Am} v + b_{Am}^2)] \]
\[ + (a / b_{Am}^2 \ln (1 + b_{Am} v / u)) / (R T^{3/2}) \]
\[ - [d(n^2 a_{Am}) / d n_i] \ln [(1 + b_{Am} v / u)] / R T^{3/2} b_{Am} - \ln Z_m \] (17)

In the above equations, \( H_m - H_{mig} / RT \) and \( S_m - S_{mig} / R \) are the mixture enthalpy departure function and mixture entropy departure function, respectively, and \( f_i \) is the fugacity of component \( i \) in a multicomponent mixture; \( b_{Am} \) and \( a_{Am} \) are defined by Eqs. 18 and 19; parameters \( a' \) and \( b' \) refer to \( (da / dT) \) and \( (db / dT) \), respectively. Expressions for the other
mixtures of methane–hydrogen sulfide at $T = 377.65 \text{ K}$ and at two different pressures. Fig. 1 shows the results of this calculation by using the present equation of state along with the PR equation (all with $k_{ij} = 0$). According to this figure, the results of calculations by the proposed equation of state are generally closer to the experimental data than the PR equation.

Another compressibility factor calculation was performed for a methane–carbon dioxide mixture ($x_{CO_2} = 0.4761$) at 250 K and at different pressures. Fig. 2 shows results of this calculation based on the present equation of state along with those obtained from the PR and SRK equations (all with $k_{ij} = 0$). According to this figure, the proposed equation of state is more accurate than the other equations reported.

A third set of compressibility factor calculations were performed for the nitrogen–carbon dioxide ($x_{CO_2} = 0.447$)

**3. Results and Discussion**

In order to test the accuracy and applicability of the present equation of state it is first used for density, enthalpy and entropy calculations of the major pure components of the sour natural gas at different temperatures and pressures. Table 2 shows results of these calculations using the present equation of state along with the SRK and PR equations. According to this table even though predictions by the SRK and PR equations are some times better than the present equation, overall the present equation of state is more accurate than the SRK and PR equations.

We have used the proposed equation of state for calculation of compressibility factors of binary
mixture at constant volume (isochore) and at different temperatures and pressures. Table 3 shows the results of this calculation as compared with the results of the PR and SRK equations of state (all with \( k_{ij} = 0 \)). According to this table, the compressibility factors calculated by the proposed equation are closer to the experimental data than the other equations.

A fourth set of compressibility factor calculations were performed for three different sour natural gas mixtures. Table 4 shows the compositions of these sour natural gas mixtures. The results of these calculations are reported in Table 5. According to this table, the compressibilities calculated using the proposed equation of state are much closer to the experimental data than the PR equation. The results obtained by using the SRK equation are equally accurate as those obtained by using the proposed equation of state.

The proposed equation of state is used for the vapor–liquid equilibria (VLE) calculations of seven different binary sour and hydrogen-containing fluid mixtures for which experimental data are available. Table 6 compares results of the VLE calculations using the present equation of state, PR equation and SRK equation assuming \( k_{ij}'s = 0 \) for all the equations. According to this table, the proposed equation of state appears to be superior to the other equations for the mixtures tested.

Figs. 3-7 show the results of the VLE calculations along with the experimental data for five different binary mixtures comprising the major components of sour natural gas systems. According to these figures, the proposed equation of state can predict thermodynamic properties of sour and hydrogen-containing vapor and liquid mixtures with good accuracy.

The calculations and comparisons reported here indicate that the proposed equation of state is quite suitable for property prediction of sour and hydrogen-containing natural gas and liquid systems of interest in the oil and gas industries. One major advantage of this equation of state is its sound theoretical basis in the choice of its mixing and combining rules and the functional forms of \( \alpha(T_r) \) and \( \beta(T_r) \) as reported by Eqs. 12 and 13. These theoretically correct choices make the proposed equation of state more suitable for extrapolation purposes than the empirical equations, beyond the ranges of the available experimental data on which equation of state parameters are based upon.

4. Notations:

- \( a \) parameter in equation of state
- \( b \) parameter in the equation of state
- \( f \) fugacity
- \( H \) enthalpy
- \( k_{ij} \) coupling parameter
- \( n \) total number of moles
- \( P \) pressure
- \( \text{PR} \) Peng-Robinson equation of state
- \( R \) Universal gas constant
- \( \text{RK} \) Redlich-Kwong equation of state
- \( S \) entropy
- \( \text{SRK} \) Soave-Redlich-Kwong equation of state
- \( T \) absolute temperature
- \( T_r = T/T_c \)
- \( v \) molar volume
- \( Z \) compressibility factor

Greek letters:

- \( \alpha \) parameter in equation of state
- \( \alpha_i \) constant
- \( \beta \) parameter in equation of state
\[ \beta_1 \text{ constant} \]
\[ \rho \text{ density} \]
\[ \pi = 3.1415927 \]
\[ \omega \text{ acentric factor} \]

**Subscripts**

A attractive

C critical

\( i,j \) component indices

ij property of \( i-j \) interaction

ig ideal gas

m mixture

r reduced

R repulsive

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**References**


