Computation of compositional grading in hydrocarbon reservoirs. Application of continuous thermodynamics

Carlos Lira-Galeana a,*, Abbas Firoozabadi a, John M. Prausnitz b

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- non-polar and polar small organic and inorganic molecules, ions, metals, polymers, surfactants, complex and biological molecules (e.g. proteins).

Theoretical techniques may comprise:

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Abstract

In a reservoir fluid column, the composition of the reservoir fluid varies from one depth to another owing to gravity forces. This problem is known as compositional grading. In the case of the plus fractions, the gravity field promotes a change in their overall composition and also their average characterization parameters will differ from one depth to another. We present a continuous thermodynamic framework for compositional grading calculations in hydrocarbon reservoirs using an equation of state. The effect of the gravity field on the segregation characteristics of the (continuous) heavy fractions of the oil is established analytically using the method of moments. This allows the molecular weight distributions of the heavy fractions to be described as a function of depth for both the oil and gas regions of a reservoir fluid column. Such monitoring is important for the case of an extreme segregation of the heavy fractions. The validity of the proposed method is demonstrated for a reservoir-fluid column where measured data is available.

Keywords: Theory; Hydrocarbon reservoir fluids; Compositional grading; Continuous mixtures; Methods of calculation

1. Introduction

Considerable variation in composition and $PVT$ properties with depth has been observed in various oil and gas-condensate fields around the world (Metcalf et al., 1988; Neveux and Sathikumar, 1988; Bath et al., 1980; Espach and Fry, 1951). For instance, bubblepoint pressure may change as much as 0.07–0.11 MPa m$^{-1}$ in an oil reservoir, while the API gravity may

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decrease 50% when the depth increases some 100 m in a heavy oil reservoir. These compositional changes (known as compositional grading) affect reserves estimation and production facility design. An extreme manifestation of compositional grading may also lead to the formation of extremely viscous oil near the water–oil contact of a given reservoir (Hirschberg, 1988).

While thermal diffusion and natural convection may affect the extent of compositional grading in hydrocarbon reservoirs (Chabak, 1992), the thermodynamic equilibrium assumption of gravity segregation provides a starting point for model development (Sage and Lacey, 1939; Wheaton, 1991). Methods for calculating compositional grading based on the use of equations of state (EOS) and the thermodynamic equilibrium concept have been proposed in the past few years (Shulte, 1980; Montel and Gouel, 1985; Wheaton, 1991). Application of these methods to reservoir-fluid columns containing heavy fractions is typically accomplished by considerable tuning of the EOS to match field data. Such tuning includes the use of \( C_{i+} \) critical properties and acentric factors as regression parameters in addition to binary interaction coefficients. Furthermore, our experience, as well as Shulte's (1980) is that the bubblepoint pressure gradient is often underestimated by a factor of three to five.

The thermodynamic equilibrium concept of gravity segregation assumes that in a multicomponent fluid column under isothermal conditions the chemical potential of the \( i \)th component in the system, \( \mu_i \), is a function of position, \( h \), according to the following differential equation (Debenedetti, 1988; Firoozabadi, 1991; Wheaton, 1991):

\[
d\mu_i = RT \, d \ln f_i = -M_i \frac{g}{g_c} \, dh \quad (i = 1, 2, \ldots, N_c)
\]  

(1)

where \( M_i \) and \( f_i \) are the molecular weight and fugacity of component \( i \), respectively, and \( h \) is positive in the upward direction. Integrating the above expression at constant temperature and molecular weight from a reference depth \( h^0 \), to a desired depth of analysis, \( h \), the following "isofugacity" condition of compositional grading is obtained:

\[
f_i(h) = f_i^0(h^0) \exp \left[ -\frac{M_i g}{RT g_c} (h - h^0) \right]
\]  

(2)

in which \( f_i^0(h^0) \) and \( f_i(h) \) are the fugacities of the \( i \)th component at the reference depth and the depth of interest, respectively.

Reservoir-fluid mixtures contain a large number of components. Application of Eq. (2) to the heavy fraction in these mixtures requires a pseudocomponent description which may result in a decrease in the amount of the heaviest pseudocomponent with depth, which is inconsistent with the concept of compositional segregation. A more realistic description of compositional grading in hydrocarbon fluid columns is to consider the composition of the heavy fraction represented by an infinite number of components, from which the use of a continuous description in Eq. (2) is more efficient. In this work, a continuous thermodynamics approach based on the method of moments is used to modify Eq. (2) for reservoir-fluid mixtures in which the molecular weight of the heavy species is the continuous characterization variable. To illustrate our method, we use an EOS of the Redlich–Kwong type. The usefulness of our approach is tested with field data for a true reservoir-fluid.
2. Compositional grading with an EOS

Hirschberg (1988) has given an illustration of the role of the plus fractions in compositional grading using the ideal-solution concept. He studied the segregation characteristics of an oil column containing asphaltenes. This section extends Hirschberg’s idea of segregation to systems containing polydisperse plus fractions.

To establish a formalism of compositional grading for polydisperse fluids, it is assumed that the reservoir-fluid column experiences segregation of components in an undersaturated liquid state. The oil composition is characterized by a set of \( k \) discrete (i.e. identifiable) light components, and one (or more) heavy-hydrocarbon ensembles (i.e. \( C_{\text{hr}} \) fraction). Then Eq. (2) is used directly for the light components; for the heavy-hydrocarbon ensemble, Eq. (2) is used within the framework continuous thermodynamics. Continuous thermodynamics is an extension of classical (i.e. finite-component) solution thermodynamics to mixtures containing very many components (Cotterman et al., 1985; Cotterman and Frausnitz, 1985; Du and Mansoori, 1986). To account for the polydisperse nature of petroleum, continuous thermodynamics replaces discrete values of composition by a continuous distribution function \( F(I) \), where \( I \) is a continuous characterization variable. A suitable variable may be, for example, the normal boiling point \( (T_b) \), or the molecular weight \( (M) \). The distribution function \( F(I) \) is normalized such that

\[
\int F(I) \, dI = 1
\]

which shows that the integral of \( F(I) \, dI \) represents the average mole fraction for species whose molecular weight falls in the range between \( I \) and \( I + dI \). Analogous to conventional phase-behavior calculations, the general problem of continuous thermodynamics is to relate the distribution function of one thermodynamic state (or phase) of the fluid to those of all other thermodynamic states (or phases) of the system.

Broadly speaking, there are two classes of continuous-thermodynamic models that represent the phase behavior of a reservoir fluid. In the first class, the same mathematical distribution function is used for all phases but the function parameters are different for each phase. One example for performing calculations is the method of moments developed by Cotterman et al. (1985); other related examples have been proposed in the literature (Lira-Galeana et al., 1991; Luks et al., 1990). The second class for performing calculations takes advantage of the orthogonal properties of the distribution functions to obtain a discretized form of the phase-equilibrium problem. One example of this second class is the Gaussian quadrature method developed by Cotterman and Frausnitz (1985). Details on applications of continuous thermodynamics can be found elsewhere (Chorn and Mansoori, 1989; Ying et al., 1989; Lira-Galeana et al., 1992).

In this work, we use the method of moments, which gives an analytical representation of the gradients of molecular weight distributions with respect to depth for heavy hydrocarbons. The method of moments has been subjected to some criticism for equilibrium calculations involving phase separation (Luks et al., 1990; Sandler and Libby, 1991). These criticisms are not relevant here. Since the method of moments is here applied to a single-phase reservoir-fluid column, material balance problems are avoided. We select the two-parameter gamma distribution
function to represent \( F(I) \). The choice of this distribution is based on its ability to represent the form of the molar distribution (i.e., mole fraction/molecular weight relationship) of true reservoir fluid mixtures (Whitson, 1983). The gamma distribution has the form

\[
F(I) = \frac{(I - \gamma)^{\alpha - 1}}{\beta^\alpha \Gamma(\alpha)} \exp\left(-\frac{I - \gamma}{\beta}\right)
\]

where \( \Gamma \) is the gamma function. In Eq. (4), \( \alpha \) and \( \beta \) determine the shape of the distribution. For gas-condensate fluids, when \( I \) is chosen equal to \( M \), \( \alpha \) is close to 1; in that event, Eq. (4) is an exponential-type distribution. Parameter \( \gamma \) fixes the origin of the distribution. The first statistical moment gives the mean, \( \theta \). A function of the second statistical moment gives the variance, \( \tau^2 \):

\[
\theta = \text{Mean} = \int_{\gamma}^{\infty} IF(I) \, dI = \alpha \beta + \gamma
\]

\[
\tau^2 = \text{Var} = \int_{\gamma}^{\infty} (I - \theta)^2 F(I) \, dI = \alpha \beta^2
\]

In Eqs. (5) and (6), \( \alpha \) is dimensionless while \( \beta \) and \( \gamma \) have the same units as \( I \).

To calculate the fugacities in Eq. (2), a suitable, yet simple EOS of the SRK form developed by Cotterman and Prausnitz (1985) (PSRK-EOS) is employed in this work. Appendix A gives a detailed description. Based on the linear dependence of the PSRK-EOS parameters \( a^{1/2} \) (energy) and \( b \) (co-volume) on hydrocarbon molecular weight, and using conventional mixing rules for these two parameters, the ratio of fugacity coefficients for each species within the \( C_{T+} \) fraction can be expressed as

\[
\frac{\Phi_i(M)}{\Phi_{II}(M)} = \exp(C^i_a + C^i_a M)
\]

where subscripts \( I \) and \( II \) refer to thermodynamic states. In Eq. (7), \( C^i_a \) and \( C^i_a \) are EOS-derived parameters that are independent of the molecular weight. The expressions for \( C^i_a \) and \( C^i_a \) can be found in Appendix B.

Using the PSRK-EOS the definition of fugacity for a species within the \( C_{T+} \) fraction whose continuous characterization variable is \( M \) is given by

\[
f(M) = \Phi(M)\eta F(M)P
\]

where \( \Phi(M) \) is the fugacity coefficient of a species with molecular weight \( M \) and \( \eta \) is the (overall) mole fraction of the continuous fraction. In Eq. (8), \( P \) is the hydrostatic pressure, while the quantity \( \eta F(M) \), represents an average mole fraction for a species with molecular weight equal to \( M \).

For the continuous fraction (i.e., the \( C_{T+} \) fraction), we replace \( f \) and \( f^0 \) in Eq. (2) by \( f(M) \) and \( f^0(M) \) (from Eq. (7)), respectively. In this way, the isofugacity condition for a species within the \( C_{T+} \) fraction is given by

\[
\eta h F_h(M) \Phi_h(M) P_h = \eta h^0 F_h^0(M) \Phi_h^0(M) P_{h^0} \exp\left[-\frac{Mg}{RT_K_c} (h - h^0)\right]
\]

To relate the first statistical moment of the distribution functions at depth \( h \) to that at depth \( h^0 \),
we multiply Eq. (9) by $M$. Because continuous thermodynamics is for a solution containing an infinite number of components, Eq. (9) is representative of a multitude of equations, one for each $M$. To determine the variation of molecular weight distribution and composition with depth, it is necessary to extend Eq. (9) to the entire $M$ domain from $\gamma$ to $\infty$ using the method of moments. The rth moment of $F(M)$, $m^r$, is defined by $m^r = \int \gamma^r M^r F(M) \; dM$. Multiplying both sides of Eq. (9) by $M$ and rearranging gives

$$
\int_{\gamma}^{\infty} M F_h(M) \; dM = \Theta_h = \left( \frac{\eta_h^o \beta_h^o}{\eta_h \beta_h} \right) \int_{\gamma}^{\infty} M F_h^o(M) \exp(C_1^o + C_2^o M) \exp(-Mb) \; dM
$$

(10)

where $b = (\gamma / RT_h)(h - h^o)$. The choice of $\gamma$ is somewhat arbitrary and directed by chemical analysis. There is no reason to change $\gamma$ with depth. Therefore we set $\gamma_h = \gamma_h^o$. To avoid higher order moments, we also set $\alpha_h = \alpha_h^o$. Carrying out the integration, we relate $F_h(M)$ to $F_h^o(M)$ through the following expressions derived from Eq. (10):

$$
\beta_h = \frac{\beta_h^o}{1 - \beta_h^o(C_2^o - b)}
$$

(11)

and

$$
\frac{\eta_h}{\eta_h^o} = \frac{P_h^o}{P_h} \exp[C_1^o + \gamma(C_2^o - b)] \left[ \frac{1}{1 - \beta_h^o(C_2^o - b)} \right]^{\eta_h^o}
$$

(12)

Eqs. (11) and (12) are the continuous thermodynamic equations analogous to Eq. (4) in the Hirschberg paper (Hirschberg, 1988). However, unlike previous formulations, Eqs. (11) and (12) relate the parameters of the distribution function at any depth to those at the reference depth by means of an EOS.

3. Computational algorithm

The calculation method described here requires simultaneous solution of $k$ isofugacity equations described by Eq. (2) for the discrete components and Eq. (12), which was derived by imposing the method of moments to the isofugacity condition for the continuous fraction. It is necessary to solve a total number of $k + 1$ simultaneous non-linear equations whose independent variables are pressure and $k$ compositions. A multidimensional Newton–Raphson algorithm can be used to solve these equations. Eq. (11) is a constraint.

Once the total algorithm has converged, the mean molecular weight of the $C_{7+}$ fraction at the depth of interest (i.e. $\Theta = \pi \beta + \gamma$) is used to pseudoize the composition of the $C_{7+}$ fraction. The pseudoization process can be performed by the quadrature method (Cotterman et al., 1986) or by the generalized properties-of-groups method proposed by Whitson (1983). The second stage of the solution algorithm is the saturation pressure computation, based on results from the pseudoization process.

The performance of the EOS in matching the field segregation data depends upon the ability of the EOS to represent the volumetric behavior of the reservoir-fluid column. Eqs. (11) and (12) provide the connection of volumetric behavior and the extent of segregation for a given hydrocarbon fraction. These two equations indicate that both the segregated mole fraction and
the distribution function parameters of the plus fraction, are strong functions of the "volumetric" parameters $C_0^b$ and $C_2^b$. The PSRK-EOS used in this work was developed from vapor pressure data of heavy hydrocarbons. We observed that incorporation of a single binary interaction coefficient between methane and the plus continuous fraction improved the volumetric accuracy of the EOS used in this work. A practical method is to adjust the binary interaction coefficient between methane and the $C_7^+$ continuous fraction to hydrostatic-pressure and composition data at a single depth. While we have used the binary interaction coefficient, an alternative method may be used to incorporate the volume translation concept (Peneloux et al., 1982), in a way suited to continuous or semicontinuous systems.

In the second part of the solution algorithm, based on the parameters of the continuous fraction, the pseudoization process is performed and the EOS is used to compute the variation of saturation pressure. Since the characterization of the heavy fraction at $h$ is different from that at $h^0$, calculation of the saturation pressure by the EOS requires methane interaction coefficients with the pseudocomponents determined from the pseudoization process. Such interaction coefficients, as expected, are similar to those obtained from VLE-based correlations.

3.1. Comparison with discrete multicomponent formalism

Prior to application to field data, it is useful to consider a comparison of the proposed method with the discrete multicomponent formalism which uses only Eq. (2). Consider a hydrocarbon liquid column at 394.4 K. The pressure at the reference depth is 30 MPa. The liquid is composed of an equimolar mixture of methane and 13 $n$-alkanes whose molecular weights fall between octane and $n$-eicosane ($n$-$C_{20}$). The compositions for the 13 $n$-alkanes used in this comparison are: (a) discrete values shown in Fig. 1, and (b) gamma distribution function shown in Fig. 2. Details of the two equivalent characterizations can be found elsewhere (Lira-Galeana et al., 1991).

Compositional-grading calculations were performed using the two procedures for a vertical distance of 500 m. For this particular application, all binary interaction coefficients between methane and each paraffin were computed as a function of the paraffin molecular weight, according to Cotterman (1985):

$$k_{C_1-M} = -0.100 + 0.309 \exp(-0.00688M)$$

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
</table>
Comparison of the proposed method with the discrete multicomponent formalism for the segregation of a mixture of methane and 13 $n$-alkanes at 394.4 K at depths of 0 m and 500 m

<table>
<thead>
<tr>
<th>Calculated property</th>
<th>Calculation method</th>
<th>Proposed method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Multicomponent</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0 m</td>
<td>500 m</td>
</tr>
<tr>
<td>Hydrostatic pressure (MPa)</td>
<td>30.0</td>
<td>27.56</td>
</tr>
<tr>
<td>Bubblepoint pressure (MPa)</td>
<td>18.36</td>
<td>19.22</td>
</tr>
<tr>
<td>Methane ( Mol% )</td>
<td>50.00</td>
<td>52.30</td>
</tr>
</tbody>
</table>
The critical properties and acentric factors for all discrete components were taken from Magoulas and Tassios (1990). Table 1 shows the calculated hydrostatic and bubblepoint pressures at the desired depth for the two methods, as well as the calculated compositional changes for methane. For the proposed method, the mean molecular weight of the continuous fraction at the reference level was used to estimate the value of $k_{C_1-M}$.

Table 1 shows that the calculated hydrostatic pressures are virtually the same for the two methods. Bubblepoint pressures and corresponding methane segregations from the two procedures are also in very good agreement.

4. Comparison with field data: East Painter reservoir

Creek and Schrader (1985) have reported segregation data for the East Painter field in the Overthrust Belt. The composition of the reservoir fluid correlates with depth such that the mole fraction of the $C_{7+}$ fraction increases from 5.7 to 8.6% over a vertical distance of 230 m. The mean molecular weight of this fraction changes substantially.
Fig. 2. Continuous composition representation for a fraction of 13 n-alkanes.

Table 2
Reservoir fluid composition for the East Painter reservoir at the reference depth ($h^0 = -1297$ m)

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0.6570</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.1120</td>
</tr>
<tr>
<td>Propane</td>
<td>0.0620</td>
</tr>
<tr>
<td>iso-Butane</td>
<td>0.0162</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.0215</td>
</tr>
<tr>
<td>iso-Pentane</td>
<td>0.0091</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>0.0083</td>
</tr>
<tr>
<td>Hexanes</td>
<td>0.0108</td>
</tr>
<tr>
<td>C$_{14}$</td>
<td>0.0859</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.0014</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.0145</td>
</tr>
</tbody>
</table>

Dewpoint pressure = 30.7 MPa
C$_5$ mean mol. weight = 158
C$_{14}$ sp. gravity = 0.796
Reservoir temperature = 361.1 K
Table 2 shows the measured composition of the reservoir fluid (well 42-7A) at the reference depth. The measured characterization parameters for the C\textsubscript{7+} fraction are molecular weight, 158 and specific gravity, 0.796. The mole percent of the C\textsubscript{7+} fraction and dewpoint pressure of the reservoir fluid at the reference depth (−1297 m subsea), are 8.6% and 30.7 MPa, respectively.

Using the C\textsubscript{7+} molecular weight and specific gravity, we estimate the parameters of the molecular weight distribution function that resemble the measured characterization properties of the C\textsubscript{7+} fraction. Whitson (1983) has shown practical procedures for obtaining these parameters from average characterization properties of the heavy fraction. The estimated mean and variance of the gamma distribution function are \( \Theta = 158 \) and \( \tau^2 = 12138 \), respectively. The molar distribution of the plus fraction is shown in Fig. 3. Based on distillation data and the relatively “light” nature of the C\textsubscript{7+} fraction, the shape of the distribution is exponential.

Creek and Schrader (1985) used a regressed Peng–Robinson-EOS (Peng and Robinson, 1976) to correlate the measured segregation properties of the East Painter reservoir. To regress the EOS, they used the measured PVT data for the reservoir fluid. No details were provided on the regression parameters and on specific data employed in the regression. Using the tuned EOS,

Fig. 3. Molar distributions of the C\textsubscript{7+} fraction of the East Painter reservoir fluid at two depths.
these authors matched the composition distribution of methane and $C_{7+}$ fraction and the saturation pressure variation.

Applying our procedure, we predicted the segregation characteristics of the East Painter reservoir fluid along a vertical distance of 230 m above the reference point. Paraffinic correlations (Cotterman et al., 1985) for determining the PSRK-EOS parameters for the continuous fraction were employed. Table 3 shows the computed methane and $C_{7+}$ composition distribution obtained from the new procedure, compared with field measurements. To compute these variations, we used a binary interaction parameter 0.15 between methane and the continuous $C_{7+}$ fraction.

Table 3 shows that the computed segregation characteristics of the oil column agree with field data for both methane and the $C_{7+}$ fraction. The predicted molecular weight variation for the $C_{7+}$ fraction, computed with Eqs. (5) and (12), agrees very well with the variation reported at field scale. Fig. 4 shows the variation.

Once the first part of the calculation has been completed, the second part of the calculation requires the pseudoization for the calculation of the saturation pressure. For this case, we used

![Diagram of molecular weights and field data](image-url)

**Fig. 4.** Variation of measured and calculated molecular weights with depth for the $C_{7+}$ fraction of the East Painter reservoir fluid.
Fig. 5. Variation of calculated and measured saturation and hydrostatic pressures with depth for the East Painter reservoir fluid.

Table 3
Measured (Creek and Schrader, 1985) and calculated segregation characteristics for the East Painter reservoir-fluid column: C<sub>7a</sub> and C<sub>1</sub> mole fraction, and C<sub>7a</sub> properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Reference depth = 0 m</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 m</td>
</tr>
<tr>
<td>C&lt;sub&gt;7a&lt;/sub&gt;</td>
<td>Molecular weight</td>
</tr>
<tr>
<td></td>
<td>T&lt;sub&gt;c&lt;/sub&gt; (K)</td>
</tr>
<tr>
<td></td>
<td>P&lt;sub&gt;c&lt;/sub&gt; (MPa)</td>
</tr>
<tr>
<td></td>
<td>ω</td>
</tr>
<tr>
<td></td>
<td>Mole fraction, data</td>
</tr>
<tr>
<td></td>
<td>Mole fraction, calc.</td>
</tr>
<tr>
<td>C&lt;sub&gt;1&lt;/sub&gt;</td>
<td>Mole fraction, data</td>
</tr>
<tr>
<td></td>
<td>Mole fraction, calc.</td>
</tr>
</tbody>
</table>
a single pseudocomponent representing the entire C7+ fraction. Table 3 presents the variation of C7+ characterization from the first part of the algorithm. This table shows that the critical properties and acentric factor of the C7+ pseudocomponent change substantially, as a result of molecular weight variation. With the characterization parameters of Table 3, the PSRK-EOS is switched to its discrete-component form, and the saturation pressure variation with depth is computed. Fig. 5 shows the results. A single interaction parameter between methane and the C7+ fraction (−0.02) suffices to give a good representation of the saturation pressure. Fig. 5 implies no gas−oil contact (GOC) for the fluid column.

5. Conclusions

The procedure outlined here takes into account the variable characteristics of the plus fractions with depth in compositional grading calculations. Application of the method of moments does not involve the material balance error when this method is used in a single-phase state. We have selected the gamma distribution function to represent the molecular weight distribution of the plus fraction of a reservoir fluid. For simplicity, only one of the two parameters of the distribution function (β) is allowed to vary with depth. Therefore, only one statistical moment must be satisfied. In view of the results presented in this paper, there may be no need to vary both α and β with depth. The method outlined above was also used to calculate the segregation characteristics of two other reservoir-fluid columns. Good agreement between data and calculated results was obtained (the results are not shown). The good agreement between calculated results and field data suggests the usefulness of the proposed model.

Acknowledgments

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List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>a</td>
<td>EOS (energy) parameter (1 MPa mol−2)</td>
</tr>
<tr>
<td>b</td>
<td>gravity modulus</td>
</tr>
<tr>
<td>b_i, b(M)</td>
<td>EOS (covolume) parameter for discrete and continuous components (1 mol−1)</td>
</tr>
<tr>
<td>C_i,2</td>
<td>EOS-derived functions in Appendix B</td>
</tr>
<tr>
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<td>fugacity of discrete component i (MPa)</td>
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List of symbols

\( a \quad \) EOS (energy) parameter (1 MPa mol\(^{-2}\))
\( b \quad \) gravity modulus
\( b_i, b(M) \quad \) EOS (covolume) parameter for discrete and continuous components (1 mol\(^{-1}\))
\( C^{1.2} \quad \) EOS-derived functions in Appendix B
\( f_i \quad \) fugacity of discrete component \( i \) (MPa)
\[ f(M) \quad \text{fugacity of continuous component (MPa)} \]
\[ F(M) \quad \text{distribution function, here taken as a gamma distribution} \]
\[ g \quad \text{acceleration due to gravity} \]
\[ g_e \quad \text{proportionality constant} \]
\[ h, h^0 \quad \text{depths of interest and reference, respectively (m)} \]
\[ i \quad \text{discrete component index} \]
\[ k \quad \text{total number of discrete (i.e. identifiable) components} \]
\[ k_{C_1-M} \quad \text{methane interaction coefficient} \]
\[ M \quad \text{molecular weight (g mol}^{-1}) \]
\[ N_e \quad \text{total number of components} \]
\[ P \quad \text{pressure (MPa)} \]
\[ P_c \quad \text{critical pressure (MPa)} \]
\[ R \quad \text{gas constant} \]
\[ T \quad \text{temperature (K)} \]
\[ T_c \quad \text{critical temperature (K)} \]

**Greek letters**
\[ \alpha, \beta, \gamma \quad \text{distribution function parameters} \]
\[ \Gamma \quad \text{gamma function} \]
\[ \Delta \quad \text{finite-difference operator} \]
\[ \eta \quad \text{overall mole fraction of a continuous fraction} \]
\[ \theta \quad \text{coefficient for temperature dependence in appendix A} \]
\[ \Theta \quad \text{first statistical moment of } F(M) \]
\[ \Phi(M) \quad \text{fugacity coefficient of continuous species} \]
\[ \omega \quad \text{acentric factor} \]

**Appendix A: the PSRK-EOS**

The fugacity coefficient of a species within a C\(_7\)_\(_{\alpha}\) fraction using the PSRK-EOS is given by

\[
RT \ln \Phi(M) = RT \ln \frac{v}{v - b} + RT \frac{b(M)}{v - b} + \frac{ab(M)}{b^2} \left( \ln \frac{v + b}{v} - \frac{b}{v + b} \right)
\]

\[
- 2 \left[ \sum_{j} \eta_j a(M, j) + \sum_{j} \sum_{i} \frac{F_j(M^+)a(M, M^+)}{b} \right] \ln \frac{v + b}{v} - RT \ln Z \quad (A1)
\]

where \( v \) and \( Z \) are the molar volume and compressibility factor of the mixture, respectively, and \( b(M) \), \( a(M, j) \) and \( a(M, M^+) \) are functions of temperature and molecular weight according to

\[ b(M) = b_0 + b_1 M \]
\[ a(M, M)^{1/2} = a_0(T) + a_1(T) M \]
\[ a(M, j) = a^{1/2}(M, M) a^{1/2}(j, j)(1 - k_{Mj}) \]
\[ a(M, M^+) = a^{1/2}(M, M) a^{1/2}(M^+, M^+)(1 - k_{MM^+}) \]
The temperature dependence for constants \( a_0(T) \) and \( a_1(T) \) is given by
\[
\begin{align*}
  a_0(T) &= \theta_1 + \theta_2 T + \theta_3 T^2 \\
  a_1(T) &= \theta_4 + \theta_5 T + \theta_6 T^2
\end{align*}
\]
where values of \( \theta_1, \theta_2, \ldots, \theta_6, \theta_7, \theta_8 \) and \( b_0 \) and \( b_1 \) parameters are given by Cotterman and Prausnitz (1985) for paraffinic, aromatic and naphthenic hydrocarbon ensembles.

The following mixing rules are used for the PSRK-EOS parameters \( a \) and \( b \):
\[
\begin{align*}
  a &= \sum_{i=1}^{k} \sum_{j=1}^{k} x_i x_j F_i(M) a(i, M) \ dM + 2 \sum_{i=1}^{k} \sum_{j=1}^{k} x_i \eta_j \int_{\gamma_i}^{\infty} F_i(M) \ dM \ dM^+ \\
  &+ \sum_{i=1}^{k} \sum_{j=1}^{k} \eta_i \eta_j \int_{\gamma_i}^{\infty} F_i(M) F_j(M^+) a(M, M^+) \ dM \ dM^+ \\
  b &= \sum_{i=1}^{k} x_i b_i + \sum_{i=1}^{k} \eta_i \int_{\gamma_i}^{\infty} F_i(M) b(M) \ dM
\end{align*}
\]

With these mixing rules, the PSRK-EOS is finally written for \( k \) discrete components and \( l \) continuous fractions as
\[
  P(T, V, n_1, n_2, \ldots, n_k, \eta_1 F_1(M), \eta_2 F_2(M), \ldots, \eta_l F_l(M)) = \frac{RT}{n - b} - \frac{a}{n(n + b)}
\]

Appendix B: expressions for evaluating the parameters in Eq. (7)

Cotterman et al. (1985) stated that Eq. (A1) can be cast as the following linear function of molecular weight:
\[
  \ln \Phi(M) = C^1 + C^2 M
\]
Explicit expressions to compute the parameters \( C^1 \) and \( C^2 \) were not reported by Cotterman et al. (1985), but they were derived in this work. The expressions are
\[
\begin{align*}
  C^1 &= b_0 \left( \frac{fb}{b} \right) - fc \left( \frac{fc}{fg} \right) a_0(T) - fd \\
  C^2 &= b_1 \left( \frac{fb}{b} \right) - fc \left( \frac{fc}{fg} \right) a_1(T)
\end{align*}
\]
where \( fb, fc, fd, \) and \( fg \) are given by
\[
  \begin{align*}
  fd &= \ln(Z - B) \\
  fg &= a(M, M)^{1/2} a(M, M^+) \\
  fe &= 2 \left[ \sum_{j} x_j a(M, j) \right] + 2 \sum_{j} \eta_j \int_{\gamma_j}^{\infty} F_j(M^+) a(M, M^+) \ dM^+
\end{align*}
\]
\[ f_d = \frac{A}{B} \left( \ln \frac{Z + B}{Z} - \frac{B}{Z + B} \right) + \frac{B}{Z - B} \]
\[ f_c = \frac{A}{B} \ln \frac{Z + B}{Z} \]
\[ A = \frac{u_P}{(RT)^2} \]
\[ B = \frac{b_P}{RT} \]

Thus, parameters \( C^1_a \) and \( C^2_a \) are simply given by
\[ C^1_a = C^1_b - C^1_a \]
and
\[ C^2_a = C^2_b - C^2_a \]

References


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Equilibrium properties: Experimental methods, data and their correlation
Transport properties

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