Fast and Robust Algorithm for Compositional Modeling: Part I—Stability Analysis Testing

Abbas Firoozabadi, SPE, and Huanquan Pan, SPE, Reservoir Engineering Research Inst. (RERI)

Summary
Given pressure, temperature, and composition of a fluid, one desires to determine whether the single phase state is stable. This problem is, in principle, much simpler than phase-behavior calculations. For certain applications, such as compositional-reservoir modeling, stability testing can be the most important item for efficient phase-behavior calculations.

In this paper, we use the tangent-plane-distance (TPD) in the reduced space to perform stability analysis testing. The results reveal that there are major advantages in the reduced space. One interesting feature of the transformation is that the TPD surface becomes smooth and has one minimum. The combination of a single minimum and the surface smoothness contributes to a remarkable robustness in calculations.

Introduction
Phase-behavior computations are an important element of thermodynamics of phase equilibria in general, and of compositional modeling of hydrocarbon reservoirs and production facilities in particular. Compositional modeling in hydrocarbon reservoirs demands robustness for hundreds of millions of phase partitioning computations with varying conditions of pressure and composition, including in the critical region.

There are five basic requirements and desirable features for phase behavior-related computations in a compositional-reservoir simulator. Given the temperature, T, the pressure, p, and the overall composition vector, \( z = (z_1, z_2, \ldots, z_i) \) one desires to:
1. Determine the phase stability.
2. Recognize the state of the phase (that is, gas or liquid).
3. Perform flash computations.
4. Calculate phase derivatives with respect to \( p \) and \( z_i \).
5. Use an adequate number of components/pseudocomponents for certain accuracy.

Item 1 above determines the need for flash calculations. When it is determined that the fluid system is in single state from stability testing, there will be no need for flash computations; flash computations are more costly and complicated than stability testing when one takes advantage of proper stability analysis testing. The TPD from stability can also be used to perform flash computations efficiently, as will be discussed in the second part of this work.

In compositional-reservoir simulators, it is necessary to recognize the phase state; one needs to know whether the single phase is a gas or a liquid phase. In Item 4 above, the total derivatives for the flow expressions are estimated. These derivatives are \( \frac{\partial f}{\partial p} \), \( \frac{\partial f}{\partial T} \), \( \frac{\partial f}{\partial n_i} \), \( \frac{\partial f}{\partial \alpha_i} \), and other similar derivatives; \( f \) is the liquid phase density, \( n_i \) is the number of moles of component \( i \) in the feed, \( n_i = (n_1, \ldots, n_{i-1}, n_{i+1}, \ldots, n_c) \), and \( c \) is the number of components. Depending on the process, sufficient accuracy may require the use of from 4 to 12 (or more) components. When the nonlinear equations in flash are performed using the Newton algorithm, the computational time is proportional to \( c^3 \). Therefore, there will be an increase of about 27 in computational time when \( c \) is increased from 4 to 12. The most important element of phase-behavior calculations in compositional modeling is, however, robustness of computations rather than speed. Robustness is the prime goal of our work.

Despite remarkable progress in the period from 1980 to 1990 in phase-behavior computations,\(^1\) a comprehensive and unified theoretical framework is yet to be developed. The results reveal that there are major advantages in the reduced space. There may be a direct link between all five, though such a link has not yet been recognized.

One major difficulty in phase-behavior computations results from the ragged shape of the Gibbs free energy surface. To be more specific, both the raggedness and the number of minima of the TPD affects the complexity of phase-behavior calculations very pronouncedly. Those issues will be discussed in detail in this paper. Another difficulty arises from the nonlinear Rachford-Rice equation, especially near the critical region. A lesser complication is the number of nonlinear equations. In this work, we will demonstrate how we can alleviate all the above complexities. This paper presents Part I of the work covering the stability analysis, which is the key item for efficient flash computations in our work. Part II will address flash computations.\(^4\)

Our algorithm is based on the reduction of the dependent variables (that is, the composition at constant \( T \) and \( p \) of the Gibbs free energy through transformation. In the following, after a brief literature review on the reduction method, we first present a new formulation of the reduction method based on the Spectral theory of linear algebra.\(^5\) Then we provide stability analysis formulation in terms of the reduction variables for the TPD,\(^6\) followed by minimization of the TPD using the simple method of Lagrange multipliers. Next, we examine the TPD surface for three-component systems for both the conventional and the reduction variables. The results for stability testing of four-multicomponent mixtures of various degrees of complexity are discussed, followed by concluding remarks.

Brief Literature Review
In 1986, Michelsen\(^7\) introduced the reduction method to perform flash calculations, assuming all interaction coefficients to be zero. With this assumption, the "\( a \)" parameter of an equation of state (EOS) such as the Peng-Robinson\(^8\) (PR-EOS) can be simplified to a single sum from a double sum. That is, with zero interaction coefficients \( \delta_{ij} \), one can write

\[
\begin{align*}
\alpha &= \sum_{m} \sum_{j} x_i a_i^{1/2} a_j^{1/2} = \left( \sum_{m} x_i a_i^{1/2} \right)^2 \\
&= \sum_{i,j} x_i x_j a_i^{1/2} a_j^{1/2}
\end{align*}
\]

As a result, the fugacity coefficient \( \varphi_i \) becomes a function of \( a_i^{1/2} \) and \( b_i \), where \( b \) is the co-volume parameter of the EOS. The equilibrium ratio \( K \), then becomes a function of parameters \( a_i^{1/2} \) and \( b_i \) of either liquid or gas, and the vapor fraction \( V \). Therefore, the computations of vapor-liquid equilibria will be related to three nonlinear equations. The assumption of zero-interaction coefficients is restrictive for reservoir fluids and may not be compensated by adjustment of parameters such as critical temperature \( T_c \), critical pressure \( p_c \), or acentric factor \( \omega \) as will be demonstrated later. Jensen and Fredenslund\(^9\) extended the work of Michelsen to
include one set of binary interaction coefficients between one component and the rest. As a result of this extension, the dependent variables were reduced to five regardless of the number of components. One of the five variables was the mole fraction of the component, for which its interaction coefficient with the other components is nonzero. In 1988, Hendricks\textsuperscript{10} presented a general approach and demonstrated that the number of variables in the fugacity coefficient can be reduced to a value less than the number of components. He used the expression for the excess Gibbs free energy and its transformation to formulate chemical potentials in terms of transformed variables. All the interaction coefficients were included in the work of Hendricks. Later, Hendricks and van Berge\textsuperscript{11} applied the procedure outlined by Hendricks\textsuperscript{10} to perform flash computations for two multicomponent mixtures. The simple Newton-Raphson algorithm was used to solve the nonlinear equations.

In a different approach, Kaul and Thrasher\textsuperscript{12} introduced a two-stage minimization of the Gibbs free energy. In the first stage, the ideal part of the Gibbs free energy is minimized, and in the second stage, the excess part is minimized; the ideal part is a function of composition, and the excess part is a function of EOS parameters. In this approach, the number of dependent variables reduces to three when the interaction coefficients are set to zero and to four with nonzero interaction coefficients. Test results show that the method is efficient with zero interaction coefficients, but inefficient with nonzero interaction coefficients.

In all the above work, the emphasis is mainly on two-phase flash. Stability testing in the reduced space and its features have not yet been explored.

**Theory of Reduction Method**

The expression for the energy parameter “$a$” of the PR-EOS and other similar equations is given by

$$a = \sum_{i=1}^{c} \sum_{j=1}^{c} x_i a_i^{1/2} q_{ij}^{1/2} (1 - \delta_{ij}). \hfill (2)$$

Let $\beta_{ij} = (1 - \delta_{ij})$; $\beta$ is the matrix with elements $\beta_{ij}$. Because $\beta$ is a symmetric matrix, we can invoke the Spectral theory of linear algebra\textsuperscript{5} for diagonalization to express it as

$$\beta = SDS^{-1} = SDS^T. \hfill (3)$$

In the above equation, the diagonal matrix is given by

$$D = \begin{pmatrix} \lambda_1 & & & & \\ & \lambda_2 & & & \\ & & \ddots & & \\ & & & \lambda_c & \\ & & & & \lambda_{c+1} \end{pmatrix}. \hfill (4)$$

and the orthogonal matrix $S$ is given by

$$S = (q^{(1)}, q^{(2)}, \ldots, q^{(c)}). \hfill (5)$$

In Eq. 4, $\lambda_1, \ldots, \lambda_c$ are the eigenvalues of $\beta$ and $q^{(1)}, \ldots, q^{(c)}$ are the corresponding eigenvectors. Each eigenvector $q^{(i)}$ is given by

$$q^{(i)} = (q_{i1}, q_{i2}, \ldots, q_{ic}). \hfill (6)$$

In Eqs. 3 and 6, $T$ represents the transpose; in Eq. 3, $S^T = S^{-1}$ because $S$ is an orthogonal matrix. In Eq. 5, $q_{i1}, \ldots, q_{ic}$ are the entries of eigenvector $q^{(i)}$. From Eq. 3, one readily obtains

$$\beta_{ij} = (1 - \delta_{ij}) = \sum_{k=1}^{c} \lambda_k q_{ik} q_{kj}. \hfill (7)$$

Combining Eqs. 2 and 7 provides

$$a = \sum_{i=1}^{c} \sum_{j=1}^{c} a_{ij}^{1/2} x_i q_{ij}^{1/2} \sum_{j=1}^{c} a_{ij}^{1/2} x_j q_{ij}. \hfill (8)$$

Let

$$q_{ii} = a_{ii}^{1/2} q_{ii}. \hfill (9)$$

Then,

$$a = \sum_{i=1}^{c} \lambda_i \sum_{j=1}^{c} x_i q_{ij}^{1/2} \sum_{j=1}^{c} x_j q_{ij}. \hfill (10)$$

Let us define $Q_i$ as

$$Q_i = \sum_{j=1}^{c} x_j q_{ij}. \hfill (11)$$

then

$$a = \sum_{i=1}^{c} \lambda_i Q_i. \hfill (12)$$

and, therefore,

$$a = a(Q_1, \ldots, Q_c). \hfill (13)$$

The compressibility factor $Z$ and the fugacity coefficient $\varphi$ are given by (see Appendix A)

$$Z = Z(Q_1, \ldots, Q_c). \hfill (14)$$

$$\varphi = \varphi(Q_1, \ldots, Q_c). \hfill (15)$$

In general, only a few eigenvalues from $\lambda_1, \ldots, \lambda_c$ are significant; most of the eigenvalues in a multicomponent mixture with a large number of components/pseudocomponents are very close to zero. Suppose for $k=m$, $\lambda_k$’s become negligible. One may, therefore, write

$$Z = Z(Q_1, \ldots, Q_{m-1}) \hfill (16)$$

$$\varphi = \varphi(Q_1, \ldots, Q_{m-1}). \hfill (17)$$

In Eqs. 16 and 17, $m$ can be much less than $c$. In the special case of zero interaction coefficients, $\delta_{ij} = 0$, $m = 1$, $\lambda_1 = 1$, and $Q = a^{1/2}$.\n
**Stability Analysis Formulation**

The stability of a given phase can be best described by the TPD.\textsuperscript{6} The TPD is simply the difference between the Gibbs free energies of a system in a single phase and in two-phase, in which the amount of the second phase for the two-phase (that is, the trial phase) is small. Because at constant $T$ and $p$ the more stable state has a lower Gibbs free energy, the single-phase state is stable if the TPD is positive.

The expression for the TPD for a multicomponent fluid is given by\textsuperscript{6}

$$\text{TPD}(y) = \sum_{i=1}^{c} y_i \mu_a(y) - \mu_a(z). \hfill (18)$$

In Eq. 18, $y = (y_1, y_2, \ldots, y_c)$ is the composition of the trial phase, and $z = (z_1, z_2, \ldots, z_c)$ is the composition of the phase for which its stability is to be determined. An alternative form of Eq. 18 can be obtained from $\varphi(z) = f_j(z, p)$ and $\varphi(y) = f_j(y, p)$, the relation between chemical potential and fugacity$^{5}$ and Eq. 18:

$$D = \sum_{i=1}^{c} y_i (\ln \varphi(y) - \ln \varphi(z)) + \sum_{i=1}^{c} y_i (\ln y_i - \ln z_i). \hfill (19)$$

In Eq. 19, the TPD is expressed in dimensionless form, $\bar{D} = (\text{TPD}/RT)$. One can use Eq. 19 to examine the stability of the fluid as the liquid phase or the stability of the fluid as the gas phase. If one is interested in testing the stability of the fluid phase with composition $z$ as a liquid, the trial phase with composition $y$ will be in gas state. On the other hand, when interested to test stability of the fluid phase with composition $z$ as the gas phase, the trial phase with composition $y$ will be in liquid state. In the process of testing the stability of a phase with composition $z$, one may find the minimum (or minima) of $\bar{D}$ (the dependent variables of $\bar{D}$ are $y$). If this minimum is negative, the fluid mixture with composition $z$ is not stable and will split into more than one phase. The above procedure suggested by Michelsen\textsuperscript{1} is currently the basis for stability analysis with the conventional variables (that is, mole fraction variables). Its implementation is not a trivial task. The method is complicated because all the minima (say, two) must be found.
Even with one minimum, the shape of the TPD will influence the search for the minimum, and the procedure may be sensitive to the initial guess.

Let us now proceed with the calculation of \( \mathbf{D} \) with the reduction variables followed by its minimization. In order to facilitate the derivations, we will examine the stability of the fluid mixture in the liquid state. (The derivations for the stability of the gas state are straightforward and follow the derivations for the stability of the liquid phase.) Eq. 19 can be rewritten for this purpose as

\[
\mathbf{D} = \sum_{r=1}^{c} y_i [\ln \phi_i - \ln \phi] + \sum_{r=1}^{c} y_i (\ln y_i - \ln z_i). \tag{20}\n\]

In Eq. 20, \( y_i \) denotes the composition of the trial vapor phase. For the purpose of finding the minimum of \( \mathbf{D} \), we will select the dependent variables as \( Q_1, \ldots, Q_m, b \), and \( y_1, \ldots, y_c \). (We have this choice: we can also assume \( \mathbf{D} \) to be a function of \( Q_1, \ldots, Q_m, b \), only.) These variables have the following constraints:

\[
\sum_{r=1}^{c} q_{awr} = Q_i \quad \alpha = 1, \ldots, m \tag{21}\n\]

\[
\sum_{r=1}^{c} y_r b_r = b \quad \gamma = 1 \tag{22}\n\]

\[
\sum_{r=1}^{c} y_r = 1 \tag{23}\n\]

From Eq. 23, \( y_r = 1 - \sum_{r=1}^{c-1} y_r \).

Let us assign \( Q_{m+1} = Q_M = b \), and \( q_{m+1} = b_r \) (see Eq. B-5) (that is, \( M = m+1 \)). Then, Eq. 20 can be written as

\[
\mathbf{D} = \sum_{r=1}^{c} y_i [\ln \phi_i - \ln \phi] + \sum_{r=1}^{c} y_i (\ln y_i - \ln z_i) + \left(1 - \sum_{r=1}^{c} y_r \right) \left[\ln \left(1 - \sum_{r=1}^{c} y_r \right) - \ln z_i \right]. \tag{24}\n\]

Eqs. 21, 22, and 23 can be represented by the following constraint:

\[
\sum_{r=1}^{c-1} q_{awr} + q_{aw} \left(1 - \sum_{r=1}^{c-1} y_r \right) = q_r \quad \alpha = 1, \ldots, M. \tag{25}\n\]

The variables of Eq. 24 are \( Q_1, \ldots, Q_m \) and \( y_r (i=1, \ldots, c-1) \), which are constrained by Eq. 25. We use the method of Lagrange multipliers to minimize \( \mathbf{D} \). One may write

\[
\ell = \mathbf{D} - \sum_{m=1}^{M} \beta_s \left[\sum_{r=1}^{c-1} q_{awr} + q_{aw} \left(1 - \sum_{r=1}^{c-1} y_r \right) - Q_r \right], \tag{26}\n\]

where \( \beta_s \) is the Lagrange multiplier.

By using \( \partial \ell / \partial y_j = 0 \) (j = 1, \ldots, c-1), one obtains (see Appendix C)

\[
\ln K_j = \left(\sum_{r=1}^{c} y_r \exp \left(\frac{M}{c} \beta_s q_{awr} \right) \right) + \left(\sum_{m=1}^{M} \beta_s q_{aw} \right) \tag{27}\n\]

The derivative of \( \ell \) (from Eq. 26) with respect to \( \beta_s \) provides

\[
Q_s = \sum_{r=1}^{c-1} q_{awr} + q_{aw} \left(1 - \sum_{r=1}^{c-1} y_r \right) \quad \gamma = 1, \ldots, M. \tag{28}\n\]

The derivative of the above expression with respect to \( y_j, j = 1, \ldots, c-1 \) gives

\[
\frac{\partial Q_s}{\partial y_j} = q_s - q_w \quad j = 1, \ldots, c-1; \gamma = 1, \ldots, M. \tag{29}\n\]

Let us denote the first two terms in Eq. 24 by \( \mathbf{D}^t \), and the remaining terms by \( \mathbf{D}^l \). Taking the derivative of \( \mathbf{D}^t \) with respect to \( y_j \) results in

\[
\frac{\partial \mathbf{D}^t}{\partial y_j} = \ln K_j - \ln K_c \quad j = 1, \ldots, c - 1. \tag{30}\n\]

Because \( \mathbf{D}^t = \mathbf{D}^l \) \((Q_1, \ldots, Q_m)\) (see Appendix B), one may write by using Eq. 30:

\[
\frac{\partial \mathbf{D}^t}{\partial y_j} = \sum_{m=1}^{M} \frac{\partial \mathbf{D}^t}{\partial y_j} = \sum_{m=1}^{M} \left(\frac{\partial \mathbf{D}^t}{\partial y_j}\right) (q_m - q_w). \tag{31}\n\]

Eqs. C-1, 30, and 31 provide the expression for the Lagrange multipliers

\[
\beta_s = \frac{\partial \mathbf{D}^t}{\partial y_j} \quad \alpha = 1, \ldots, M. \tag{32}\n\]

Next we will discuss the algorithm to obtain the minimum of the TPD.

The dimensionless TPD can also be cast into the following form, \( \mathbf{D} = \mathbf{D}(Q_1, \ldots, Q_m) \).

The minimum of \( \mathbf{D} \) is simply given by

\[
\nabla \mathbf{D} = 0. \tag{33}\n\]

Using the Newton algorithm,

\[
\nabla \mathbf{D}_x = \nabla \mathbf{D}_y + \nabla \mathbf{D}_z \delta Q^y = 0. \tag{34}\n\]

Eq. 35 is written in vector form; \( \nabla \mathbf{D}_x \) is the Hessian matrix \( \mathbf{H} \) defined by

\[
\mathbf{H} = \frac{\partial^2 \mathbf{D}}{\partial (\delta Q^y)^2}, \tag{36}\n\]

which is an \( M \times M \) matrix.

The iterative expression for the estimation of \( \delta Q^y \) reads

\[
\mathbf{H} \delta Q^y = -\nabla \mathbf{D}/\delta Q^y. \tag{37}\n\]

Earlier we divided \( \mathbf{D} \) into \( \mathbf{D}^t \) and \( \mathbf{D}^l \). We can also divide the Hessian matrix into the corresponding parts \( \mathbf{H}^t \) and \( \mathbf{H}^l \) given by

\[
\mathbf{H}^t = \frac{\partial^2 \mathbf{D}^t}{\partial (\delta Q^y)^2} \quad \text{and} \quad \mathbf{H}^l = \frac{\partial^2 \mathbf{D}^l}{\partial (\delta Q^y)^2}. \tag{38}\n\]

From Eq. 32 and the definition of \( \mathbf{H}^l \) above,

\[
\mathbf{H}^l = \frac{\partial^2 \mathbf{D}^l}{\partial (\delta Q^y)^2} = \frac{\partial \mathbf{H}^t}{\partial (\delta Q^y)^2}, \tag{39}\n\]

which can be approximated by

\[
\Delta \mathbf{H} = \nabla \mathbf{H} [\mathbf{H}^{l-1}] \Delta \mathbf{Q}^y. \tag{40}\n\]

Combining Eqs. 37 and 39 provides the iterative expression for the minimization of the TPD,

\[
(I + \mathbf{H}^{(l-1)})^{-1} \Delta \mathbf{Q}^y = \delta \mathbf{Q}^y. \tag{41}\n\]

The elements of \( \mathbf{H}^{(l-1)} \) are obtained from Eq. C-1 from the data in Steps 1 and 2 using the linear-least squares for the first iteration.

4. The equilibrium ratios \( \mathbf{K} \) are obtained from Eq. 27 in subsequent iterations.

5. Then \( y \) are calculated from \( y = \mathbf{K} \mathbf{e} \) and \( Q^y (\alpha = 1, \ldots, M) \) are calculated from \( Q^y = \sum_{j=1}^{c-1} q_{awr} \).
6. The convergence of the Lagrange multipliers $\beta_n$ is examined. If convergence criterion of, say, $\|\Delta\beta\|<10^{-6}$ is not met, Eq. 40 is used to update $\beta_n$ and one goes back to Step 4.

The eigenvalues and the eigenvectors in Step 1 are calculated by transforming the symmetric matrix $\beta$ into a tridiagonal matrix, and then computing the eigenvalues and eigenvectors of the tridiagonal matrix. The Gaussian elimination is used without the pivot computation to solve the linear equations in Step 6. To our surprise, as will see next and in the results section, the simple Newton algorithm in conjunction with the above procedure with the reduction variables is extremely robust. Next we will examine the shape of the TPD surface.

**TPD Surface.** The shape and smoothness of the TPD surface affects considerably the number of iterations and the robustness of an iterative process for locating the minimum (minima). In the course of this work, we were pleasantly surprised that the calculation of the minimum of the TPD with the reduction variables is a simple task. This experience is completely different from the work of others who have found the calculation of the minima of TPD with conventional variables (that is, mole fractions) to be complicated. Perhaps the best way to appreciate the merit of our approach for stability testing is the visual examination of the TPD surface with and the reduction variables. The minimum is the same as the conventional variables. This can be done in a 3D space for ternary mixtures only; in a three-component mixture, one can examine the TPD vs. mole fraction of components 1 and 2 in the trial phase. The plot of the TPD with conventional variables (that is, mole fractions) to be a simple task. This experience is completely different from the calculation of the minimum of the TPD with the reduction variables.

**Fig. 1** shows the TPD vs. the reduction variables $a^{1/2}$ and $b$ and the conventional variables $x_C$ and $x_{nC_10}$ both of the vapor trial phase. We are interested in determining the stability of the $C_1/nC_10/nC_{10}$ system at 300 K and 100 bar with $z_C=0.80$, $z_{nC_10}=0.10$, $z_{nC_{10}}=0.10$ as a liquid. This time, there are two minima with the conventional variables for the TPD. These minima are −0.047 and −0.201. However, in the reduced space, there is only one minimum, which is −0.201. In the reduced space, it takes only five iterations to obtain the minimum using the procedure outlined above. The negative minimum in both the conventional space and the reduced space implies that the assumed liquid phase is not stable.

**Fig. 4** depicts the TPD vs. the reduction variables and the conventional variables for a mixture of $z_C=0.10$, $z_{nC_10}=0.40$, $z_{nC_10}=0.50$ at $T=300$ K, and $p=100$ bar. The minimum is zero for the assumed liquid state. This is the so-called trivial solution. In the reduced space, it takes only three Newton iterations to establish that the trial vapor phase has the same composition as the assumed liquid phase. Note that in the conventional space, the surface is not smooth for large values of TPD.

**Fig. 5** shows the dimensionless TPD vs. the reduction variables and the conventional variables for the $C_1/nC_10/nC_{10}$ system at 300 K and 100 bar for $z_C=0.998$, $z_{nC_10}=0.0012$, $z_{nC_{10}}=0.0008$. As with all the above ternary mixtures, we tested the stability for the initial liquid state, and, therefore, the variables in Fig. 5 correspond to the trial vapor phase. There is one minimum in both spaces; this minimum is zero, implying the trivial solution. Note that for the reduction variables, the TPD surface is very smooth in comparison with the conventional variables. It took four Newton iterations to calculate the minimum in the reduced space based on the procedure outlined earlier. We also performed the stability of this ternary system assuming the initial gas state. A minimum TPD = 0.078 was calculated in six iterations in the reduced space, implying that the initial state of gas is stable.

**Results**

We use four mixtures in our stability testing to demonstrate the robustness and efficiency of our proposed method. The test mixtures include:

- Synthetic oil
- Synthetic oil/CO$_2$ mixture

![Fig. 1—Dimensionless TPD vs. $x_C$ and $x_{nC_{10}}$ for the $C_1/nC_{10}/CO_2$ system at 350 K and 50 bar: $z_C=0.40$, $z_{nC_{10}}=0.30$, and $z_{CO_2}=0.30$.](image-url)
• Billings crude/natural gas mixture\textsuperscript{15}
• Kilgrin gas condensate (see Table 1).\textsuperscript{16}

The critical properties of all the pseudocomponents are estimated using the Cavett correlations.\textsuperscript{17} The nonzero binary interaction coefficients are listed in Tables 2 through 4. Tables 3 and 4 provide the critical properties and the acentric factor of all components/pseudocomponents. The interaction coefficients are obtained from Katz and Firoozabadi\textsuperscript{18} and by matching the saturation pressure to estimate the interaction coefficient between C\textsubscript{t} and the residue. Table 5 lists the nonzero eigenvalues from the matrix \( \mathbf{B} \) for all the mixtures. We use stability analysis to calculate the saturation pressure by decreasing the pressure with an increment of 0.1 bar at

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Dimensionless TPD vs. \( a^{1/2} \) and \( b \) for the C\textsubscript{t}/nC\textsubscript{10}/CO\textsubscript{2} system at 350 K and 50 bar: \( z_{C_t}=0.40, \ z_{nC_{10}}=0.30, \) and \( z_{CO_2}=0.30. \)}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Dimensionless TPD vs. the reduction and conventional variables for the C\textsubscript{t}/nC\textsubscript{5}/nC\textsubscript{10} system at 300 K and 100 bar: \( z_{C_t}=0.80, \ z_{nC_5}=0.10, \) and \( z_{nC_{10}}=0.10. \)}
\end{figure}
constant temperature until the mixture changes its state from single-phase to two-phase. The results are presented in the following.

Synthetic Oil (Mixture I). First, the conventional method is used to calculate the saturation pressure with ten components. Then, the stability testing from the reduction method is employed. There are three nonzero eigenvalues (see Table 5); $m/H_{11505} = 3$, $m/H_{11505} = 2$, and $m/H_{11505} = 1$ represent the number of eigenvalues in the descending order; $m = 1$ represents the use of all three eigenvalues; and for $m = 1$, the largest eigenvalue is used in stability calculations. The stability testing with zero interaction coefficients is also performed with and without the adjustment of the critical temperature of nC$_{10}$. The measured bubblepoint pressure at 322 K is used to adjust the critical temperature of nC$_{10}$.

The saturation pressures are plotted in Fig. 6. The results for $m = 3$ are identical to those of the conventional method (not shown in the figure). The figure shows that for $m = 2$, with three variables, the stability testing provides a very good approximation for the entire range; $m = 1$, which has two variables in stability testing, does not give reasonable prediction at temperatures below 540 K. For $\delta = 0$, the deviations at low temperatures are greater than for $m = 1$ in view of the fact that both methods have two variables. The adjustment of $T_c$ for nC$_{10}$ to match the bubblepoint pressure at 322 K increases the value of $T_c$ from 617.9 to 745 K. The approach produces the worst results (see Fig. 6).

Table 6 provides the number of iterations at different saturation pressures. The convergence criterion of $1 \times 10^{-6}$ was used in the calculations (see Step 6 of the computation procedure). The results show that the number of iterations depends mainly on the distance from the critical point (CP). The closer to the CP, the greater the number of iterations. The number of iterations is two times higher in the critical region than outside the region.
Fig. 7 depicts the number of iterations vs. pressure at 572.5 K for $m = 2$ and $m = 1$. The results further show that the number of iterations is only two times higher in the near-critical point and critical point than it is far away from the region.

We have made a number of tests to evaluate the execution time for $m = 1$, $m = 2$, and $m = 3$. The results show about one-third of CPU time is saved if $m = 2$ is used rather than $m = 3$; $m = 3$ has four variables, and $m = 2$ has three in the reduction method. Ten variables are required to perform stability analysis in the conventional method.

Synthetic Oil/CO$_2$ Mixture (Mixture II). CO$_2$ often complicates the calculation of phase behavior of crude oils. The main reasons are its molecular features and physical properties, which are different from those of hydrocarbons. Therefore, the stability analysis for CO$_2$/crude mixtures should be examined. The complication for two-phase region predictions in the reduction method may be mainly because of the interaction coefficients. There are five nonzero eigenvalues for the matrix $F$; the values are listed in Table 5. $m = 5$, $m = 4$, $m = 3$, $m = 2$, and $m = 1$ represent the stability calculations with five, four, three, two, and one eigenvalue(s), respectively. Note that $m = 5$ and the conventional method give the same results. As with the designation in the synthetic oil, $\delta = 0$ represents the calculations with zero-interaction coefficients.

Fig. 8 depicts the predicted saturation pressure vs. mole percent of CO$_2$ at 322 K. Note that the results for $m = 4$ are very close to the conventional method; $m = 3$ (four variables) provides a good approximate, while $m = 2$ (three variables) produces fair results. For $m = 1$ (two variables), there is a large deviation implying that the second eigenvalue in Table 5 cannot be neglected. The results for $\delta = 0$ are inaccurate. With $\delta = 0$, when $T_c$ of nC$_{10}$ is adjusted to match the saturation pressure at $x_{CO_2} = 0.60$ and 322 K, a wrong trend is predicted (true value of $T_c$ of nC$_{10} = 617$ K, adjusted value $= 930$ K).

Table 7 lists the number of iterations at different CO$_2$ concentrations. As with the results for the synthetic oil, the number of iterations in the critical region is approximately twice what it is away from the CP. The number of iterations depends on the distance from the CP; it is independent of the number of eigenvalues.

Billings Crude/Natural Gas Mixture (Mixture III). First, C$_{27}$ is characterized using the distillation data. Then, the conventional method is used to perform flash calculations at 366.48 K for various pressures. The composition of liquid phase is used to compute bubblepoint pressure from stability testing; therefore, the bubble-point pressure should be the same as flash pressure. As with the synthetic oil, there are three nonzero eigenvalues (see Table 5); $m = 3$, $m = 2$, and $m = 1$ represent three, two, and one eigenvalue, respectively. Fig. 9 plots the results, which are very similar to those in the synthetic oil; $m = 3$ and the conventional method are identical (not shown); $m = 2$ provides an excellent approximation, while $m = 1$ gives a large deviation.

Kilgin Gas Condensate (Mixture IV). Mixture IV is a very complex gas condensate. It contains nonhydrocarbon components N$_2$ and CO$_2$. There are six nonzero eigenvalues for this mixture. Fig. 10 plots the saturation pressure vs. temperature. The conventional method, and $m = 6$, produce identical results as expected; $m = 5$ also produces excellent results ($m = 6$ and $m = 5$ are not shown); $m = 4$ and $m = 3$ provide very good approximation. However, $m = 2$ and $m = 1$ give large deviations, and $m = 1$ produces better results than $\delta = 0$ (both have two independent variables).

Comparison of the Conventional and Reduction Methods

Michelsen’s method for stability analysis, which is based on locating the stationary points of the TPD in the conventional space, can be used in conjunction with the successive substitution (SS), the Newton algorithm, or the combination of the SS and Newton’s algorithm. Unlike the reduction method of this study, the Newton algorithm for the conventional stability analysis has poor convergence when Wilson’s correlation is used to initialize the iterations. In this work, we compare our reduction approach with the conventional method using the combined SS and Newton’s method of solution. In the conventional method, the SS method is used first. When the Euclidean norm of step-length vector is less than $10^{-2}$, the iteration switches to Newton’s method. Analytical Jacobian matrix is used for Newton’s method in the conventional stability. Table 8 presents the performance of our reduction method and the conventional method for Mixtures III and IV. Note that the Newton method always converges in our approach; for the conventional method, both the number of iterations and convergence depend on the switching criterion from the SS to the Newton method. For both methods, as the critical point is approached, the number of iterations increases. Considering that the reduction method is very robust, that the number of variables in the conventional approach can be much more than the reduction approach, that the search for the second minimum in the conventional approach is a nontrivial task, and, finally, that the total number of iterations in the conventional method is higher than that of the reduction method, one may readily conclude the superiority of our proposed approach. (According to Abbvani and Beaumont, one SS iteration =0.7 Newton iteration.)

We also compared our formulation with the results from the formulation of Jensen and Fredenslund, in which our approach...
m = 3 was used. Because the transformation from Ref. 9 has four variables for stability, then the comparison between ours and that of the Jensen-Fredenslund transformation is on the same basis. We found our approach to be more accurate. The results for Mixture II were only used in this comparison.

**Discussion and Concluding Remarks**

The algorithm presented in this paper for stability analysis has several important merits. It is very flexible in terms of speed and accuracy. One can truncate after a small eigenvalue; two eigenvalues were used for the synthetic oil and the Billings crude/natural gas mixture with good approximations. The zero-interaction coefficient methodology cannot be recommended, as was demonstrated with three examples. The speed and the convergence in our procedure is independent of the value of the interaction coefficients. This experience is different from the work reported in Ref. 12, in which the efficiency of calculations strongly becomes a function of interaction coefficients.

The most important feature of our proposed method for stability analysis is its robustness. Our numerical experience with the mixtures presented in this paper and a number of other complex mixtures reveals that the approach is very robust. After examination of Figs.1 through 5, one may conclude that the transformation in the reduced space reduces considerably the raggedness of the TPD surface. This feature, together with the property of only one minimum, gives huge advantage to our approach in comparison to the conventional approach. Another important feature of the proposed approach is that one can include all the interaction coefficients which are essential, especially for CO2-crude mixtures.

**Nomenclature**

- $a$ = energy parameter of the EOS
- $A$ = defined by Eq. A-2
- $b$ = covolume parameter

**Figure 6—P-T diagram for Mixture I.**

**Table 4—Composition, Critical Properties, $\omega$ and $\delta g$ for Mixture IV**

<table>
<thead>
<tr>
<th>Comp.</th>
<th>mol (%)</th>
<th>MW</th>
<th>$T_c$ (K)</th>
<th>$P_c$ (bar)</th>
<th>$\omega$</th>
<th>$\delta_{N_2-C_1}$</th>
<th>$\delta_{CO_2-C_1}$</th>
<th>$\delta_{C_1-C_1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2</td>
<td>0.19</td>
<td>28.01</td>
<td>126.2</td>
<td>33.5</td>
<td>0.04</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CO2</td>
<td>1.01</td>
<td>44.01</td>
<td>304.2</td>
<td>72.8</td>
<td>0.225</td>
<td>-0.02</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C1</td>
<td>86.49</td>
<td>16.04</td>
<td>190.6</td>
<td>45.4</td>
<td>0.008</td>
<td>0.12</td>
<td>0.093</td>
<td>0</td>
</tr>
<tr>
<td>C2</td>
<td>2.48</td>
<td>30.07</td>
<td>305.4</td>
<td>48.2</td>
<td>0.098</td>
<td>0.12</td>
<td>0.128</td>
<td>0</td>
</tr>
<tr>
<td>C3</td>
<td>1.28</td>
<td>44.1</td>
<td>368.9</td>
<td>41.9</td>
<td>0.152</td>
<td>0.12</td>
<td>0.123</td>
<td>0</td>
</tr>
<tr>
<td>nC4</td>
<td>0.72</td>
<td>58.12</td>
<td>408.1</td>
<td>36.0</td>
<td>0.176</td>
<td>0.12</td>
<td>0.136</td>
<td>0.02</td>
</tr>
<tr>
<td>nC5</td>
<td>0.37</td>
<td>58.12</td>
<td>425.2</td>
<td>37.5</td>
<td>0.193</td>
<td>0.12</td>
<td>0.125</td>
<td>0.02</td>
</tr>
<tr>
<td>nC6</td>
<td>0.22</td>
<td>72.15</td>
<td>460.4</td>
<td>33.4</td>
<td>0.227</td>
<td>0.12</td>
<td>0.131</td>
<td>0.025</td>
</tr>
<tr>
<td>nC7</td>
<td>0.14</td>
<td>72.15</td>
<td>469.6</td>
<td>33.3</td>
<td>0.251</td>
<td>0.12</td>
<td>0.12</td>
<td>0.025</td>
</tr>
<tr>
<td>C6-C9</td>
<td>0.9978</td>
<td>103.56</td>
<td>547.4</td>
<td>30.3</td>
<td>0.410</td>
<td>0.12</td>
<td>0.12</td>
<td>0.035</td>
</tr>
<tr>
<td>C10-C14</td>
<td>1.259</td>
<td>161.99</td>
<td>643.8</td>
<td>22.9</td>
<td>0.670</td>
<td>0.12</td>
<td>0.12</td>
<td>0.038</td>
</tr>
<tr>
<td>C15-C19</td>
<td>1.2321</td>
<td>233.97</td>
<td>724.2</td>
<td>17.0</td>
<td>0.930</td>
<td>0.12</td>
<td>0.12</td>
<td>0.038</td>
</tr>
<tr>
<td>C20-C24</td>
<td>0.9024</td>
<td>302.66</td>
<td>777.4</td>
<td>13.4</td>
<td>1.160</td>
<td>0.12</td>
<td>0.12</td>
<td>0.038</td>
</tr>
<tr>
<td>C25+</td>
<td>2.7087</td>
<td>437.75</td>
<td>849.6</td>
<td>9.9</td>
<td>1.604</td>
<td>0.12</td>
<td>0.12</td>
<td>0.038</td>
</tr>
</tbody>
</table>

**Table 5—Nonzero Eigenvalues for Test Mixtures**

<table>
<thead>
<tr>
<th>No.</th>
<th>Mixture I</th>
<th>Mixture II</th>
<th>Mixture III</th>
<th>Mixture IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.95735</td>
<td>10.7487</td>
<td>10.9783</td>
<td>13.562</td>
</tr>
<tr>
<td>2</td>
<td>0.0706504</td>
<td>0.220662</td>
<td>0.05008</td>
<td>0.4177</td>
</tr>
<tr>
<td>3</td>
<td>-0.0280032</td>
<td>0.0642569</td>
<td>-0.02837</td>
<td>0.07158</td>
</tr>
<tr>
<td>4</td>
<td>-0.0327679</td>
<td>-0.04311</td>
<td>-0.01329</td>
<td>0.005196</td>
</tr>
<tr>
<td>5</td>
<td>-0.000864411</td>
<td>-0.01329</td>
<td>0.005196</td>
<td>0.005196</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td>0.005196</td>
</tr>
</tbody>
</table>

$B$ = defined by Eq. A-3
$c$ = number of components
$C$ = matrix with elements $C_{ik}$
$\mathbf{D}$ = dimensionless TPD
$\mathbf{D}$ = diagonal matrix with diagonal elements
$\mathbf{F}$ = defined by Eqs. B-2 and B-6
$H$ = Hessian matrix
$K$ = equilibrium ratio
$m$ = number of significant eigenvalues
$M$ = $m$+1
$p$ = pressure
$q$ = eigenvector elements
$R$ = gas constant
$S$ = diagonal matrix
$T$ = temperature
$U$ = matrix with elements given by Eq. D-4
$x$ = mole fraction
$y$ = mole fraction
$z$ = mole fraction
$Z$ = compressibility factor
$\varphi$ = fugacity coefficient
$\mu$ = chemical potential
$\omega$ = acentric factor
$\delta$ = Kronecker delta, also binary interaction coefficients
Subscripts
i, j, k, l = component index, also derivative index

Superscripts
L = liquid phase index
V = vapor phase index

Acknowledgments
We thank Dr. Bret Beckner of Mobil Technology Corp. (now with ExxonMobil Upstream Research Co.) for providing the opportunity to work on this project. We also appreciate many interesting discussions and suggestions from Dr. Kenneth M. Brantferger of Mobil Technology Corp. (now with ExxonMobil Upstream Research Co.). Dr. K. Ghorayeb of RERI performed the plotting of the data in Figs. 1 through 5 with remarkable skill. His help is much appreciated.

References

![Table 6](image)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>m = 3</th>
<th>m = 2</th>
<th>m = 1</th>
<th>δ = 0</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>322</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>339</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>370</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>400</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>430</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>460</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>490</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>520</td>
<td>8</td>
<td>8</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>540</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>550</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>565</td>
<td>11</td>
<td>11</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>575</td>
<td>12</td>
<td>12</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>580</td>
<td>10</td>
<td>10</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>583*</td>
<td>8</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>583**</td>
<td>7</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>583.6*</td>
<td>8</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>583.6**</td>
<td>7</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>580</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>575</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>

\( T_c = 571.82 \) K \( p_c = 79.47 \) bar
\( T_c = 571.43 \) K \( p_c = 78.23 \) bar

* retrograde dewpoint
** dewpoint

![Table 7](image)

<table>
<thead>
<tr>
<th>CO₂% (mole)</th>
<th>m = 3</th>
<th>m = 2</th>
<th>m = 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>20</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>40</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>50</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>60</td>
<td>6</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>70</td>
<td>8</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>75</td>
<td>9</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>80</td>
<td>12</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>85</td>
<td>13</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>90</td>
<td>17</td>
<td>17</td>
<td>15</td>
</tr>
<tr>
<td>93.3</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>95</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>97.5</td>
<td>7</td>
<td>7</td>
<td>7</td>
</tr>
</tbody>
</table>

Fig. 7—Number of Newton’s iterations vs. pressure at 572.5 K for Mixture I.

Fig. 8—Saturation pressure vs. CO₂ concentration at 322 K for Mixture II.

![Diagram](image)


**Table 8**—Number of Iterations for Stability Testing in the Reduction and Conventional Methods

<table>
<thead>
<tr>
<th>p (bar)</th>
<th>Reduction</th>
<th>Conventional</th>
<th>Reduction</th>
<th>Conventional</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,000</td>
<td>2 Newton</td>
<td>*</td>
<td>3,000</td>
<td>2 *</td>
</tr>
<tr>
<td>2,000</td>
<td>6 Newton</td>
<td>11 SSI</td>
<td>2,000</td>
<td>2 *</td>
</tr>
<tr>
<td>1,500</td>
<td>6 Newton</td>
<td>14 SSI</td>
<td>1,500</td>
<td>8 27 2</td>
</tr>
<tr>
<td>1,000</td>
<td>7 Newton</td>
<td>26 SSI</td>
<td>1,400</td>
<td>8 32 2</td>
</tr>
<tr>
<td>800</td>
<td>8 Newton</td>
<td>59 SSI</td>
<td>1,300</td>
<td>8 40 2</td>
</tr>
<tr>
<td>750</td>
<td>10 Newton</td>
<td>108 SSI</td>
<td>1,200</td>
<td>9 55 2</td>
</tr>
<tr>
<td>740</td>
<td>10 Newton</td>
<td>132 SSI</td>
<td>1,100</td>
<td>11 116 2</td>
</tr>
<tr>
<td>730</td>
<td>11 Newton</td>
<td>168 SSI</td>
<td>1,080</td>
<td>11 168 2</td>
</tr>
<tr>
<td>720</td>
<td>13 Newton</td>
<td>150 SSI</td>
<td>1,060</td>
<td>16 411 4</td>
</tr>
<tr>
<td>710</td>
<td>11 Newton</td>
<td>96 SSI</td>
<td>1,052</td>
<td>12 112 3</td>
</tr>
<tr>
<td>705</td>
<td>10 Newton</td>
<td>81 SSI</td>
<td>1,050</td>
<td>11 104 3</td>
</tr>
<tr>
<td>700</td>
<td>10 Newton</td>
<td>71 SSI</td>
<td>1,045</td>
<td>11 83 2</td>
</tr>
<tr>
<td>695</td>
<td>10 Newton</td>
<td>63 SSI</td>
<td>1,040</td>
<td>10 74 2</td>
</tr>
<tr>
<td>690</td>
<td>10 Newton</td>
<td>57 SSI</td>
<td>1,020</td>
<td>11 49 2</td>
</tr>
<tr>
<td>685</td>
<td>9 Newton</td>
<td>52 SSI</td>
<td>100</td>
<td>9 38 2</td>
</tr>
<tr>
<td>680</td>
<td>9 Newton</td>
<td>48 SSI</td>
<td>900</td>
<td>8 20 2</td>
</tr>
<tr>
<td>670</td>
<td>9 Newton</td>
<td>42 SSI</td>
<td>800</td>
<td>7 14 1</td>
</tr>
<tr>
<td>660</td>
<td>9 Newton</td>
<td>37 SSI</td>
<td>700</td>
<td>7 10 1</td>
</tr>
<tr>
<td>640</td>
<td>8 Newton</td>
<td>30 SSI</td>
<td>600</td>
<td>6 8 1</td>
</tr>
<tr>
<td>600</td>
<td>8 Newton</td>
<td>23 SSI</td>
<td>500</td>
<td>6 7 1</td>
</tr>
<tr>
<td>500</td>
<td>7 Newton</td>
<td>14 SSI</td>
<td>400</td>
<td>5 6 1</td>
</tr>
<tr>
<td>400</td>
<td>6 Newton</td>
<td>10 SSI</td>
<td>300</td>
<td>5 5 1</td>
</tr>
<tr>
<td>200</td>
<td>5 Newton</td>
<td>6 SSI</td>
<td>200</td>
<td>5 4 1</td>
</tr>
</tbody>
</table>

* does not converge
The PR-EOS in terms of $y$ can be written as


(A-1)

where

$$A = \frac{ap}{(RT)^3} \quad \text{...........................................} \quad (A-2)$$

and

$$B = \frac{bp}{(RT)^2} \quad \text{...........................................} \quad (A-3)$$

Note that according to Eq. A-1, once A and B are provided, Z can be determined: $Z = Z(A, B)$. Using Eq. 13, one can then readily derive Eq. 14 of the text.

The expression for fugacity coefficient of component $i$ is given by

$$\ln\varphi_i = \frac{b_i}{b}(Z - 1) - \ln(Z - B)$$

(A-4)

The term $\sum_{j=1}^{m} \phi_j^i (1 - \delta_{ij})$ can be expressed as

$$\sum_{j=1}^{m} \phi_j^i (1 - \delta_{ij}) = \sum_{j=1}^{m} \lambda_j q_j = \sum_{j=1}^{m} \lambda_j q_j$$

(A-5)

by combining Eqs. 7, 9, and 11. Eqs. A-4 and A-5 establish Eq. 17 of the text.

**Appendix B: Expressions for $\bar{D}'$ and $\bar{D}''$**

The first term of the TPD in Eq. 20 is denoted by $\bar{D}'$ and is given by

$$\bar{D}' = \sum_{i=1}^{n} y_i [\ln \varphi_i^1(y) - \ln \varphi_i^1(z)]. \quad \text{...........................................} \quad (B-1)$$

Let us further subdivide the two terms in Eq. B-1. The first term in Eq. B-1 is denoted by $\bar{D}''$ and is expressed by

$$\bar{D}'' = \sum_{i=1}^{n} y_i \ln \varphi_i^1(y). \quad \text{...........................................} \quad (B-2)$$

Substitution of Eq. A-4 into Eq. B-2 provides the expression for $\bar{D}''$ which reads

$$\bar{D}'' = (Z' - 1) - \ln(Z' - B') = \frac{A''}{2\sqrt{2B''}} \ln \frac{Z' + 2.414B''}{Z' - 0.414B''}. \quad \text{...........................................} \quad (B-3)$$

Note that according to the above expression,

$$\bar{D}'' = \bar{D}''(Q_1', Q_2', B_1') = \bar{D}''(Q_1', Q_2', b_1'). \quad \text{...........................................} \quad (B-4)$$

Let us denote the second term in Eq. B-1 by $\bar{D}'$

$$\bar{D}' = \sum_{i=1}^{m} y_i \ln \varphi_i^1(z). \quad \text{...........................................} \quad (B-5)$$

Substitution of Eq. 5 A-5 into Eq. B-5 provides

$$\bar{D}' = \frac{b'}{b'} (Z' - 1) - \ln(Z' - B')$$

$$= \frac{A'}{2\sqrt{2B'}} \ln \frac{Z' + 2.414B'}{Z' - 0.414B'}. \quad \text{...........................................} \quad (B-6)$$

Note that according to Eq. B-6,

$$\bar{D}'' = \bar{D}''(Q_1', Q_2', b_1') = \bar{D}''(Q_1', Q_2', b_1'). \quad \text{...........................................} \quad (B-7)$$

$\bar{D}'$ (the second term of the TPD in Eq. 20) is only a function of $y$. Because $K_i = K_i(Q_1', Q_2', b_1')$, one readily finds

$$\bar{D}'' = \bar{D}''(Q_1', Q_2', b_1'). \quad \text{...........................................} \quad (B-8)$$

**Appendix C: Expression for $K$**

From $\partial \psi/\partial y_j = 0$ and Eq. 26,

$$\ln K_j - \ln K = \sum_{j=1}^{n} \beta_j q_j - q_m \quad j = 1, \ldots, c - 1 \quad \text{...........................................} \quad (C-1)$$

The above equation can be also expressed as

$$y_j = \frac{\exp \left[ \sum_{i=1}^{n} \beta_i q_i \right]}{\sum_{i=1}^{n} \beta_i q_i} \quad j = 1, \ldots, c - 1 \quad \text{...........................................} \quad (C-2)$$

$K_j$ can be expressed by

$$K_j = \frac{1 - \sum_{j=1}^{c} y_j}{z}, \quad j = 1, \ldots, c - 1 \quad \text{...........................................} \quad (C-3)$$

Introducing $y_j$ from Eq. C-2 into Eq. C-3,

$$\ln K_j = \frac{1}{z_1} \left[ \exp \left[ \sum_{i=1}^{n} \beta_i q_i \right] \right] + \sum_{i=1}^{n} \beta_i q_i \quad \text{...........................................} \quad (C-4)$$

From Eqs. C-1 and C-4,

$$\ln K_j = \left[ \sum_{i=1}^{n} \beta_i q_i \right] + \sum_{i=1}^{n} \beta_i q_i \quad j = 1, \ldots, c - 1 \quad \text{...........................................} \quad (C-5)$$

Eq. 27 of the text is from Eqs. C-4 and C-5.

**Appendix D: Hessian Matrix $H = H^2 + H^4$**

The matrix $H^4$ is given by

$$H^4 = \left[ \begin{array}{cccc} \frac{\partial^2 \bar{D}''}{\partial Q_1^2} & \frac{\partial^2 \bar{D}''}{\partial Q_1 \partial Q_2} & \cdots & \frac{\partial^2 \bar{D}''}{\partial Q_1 \partial Q_m} \\ \frac{\partial^2 \bar{D}''}{\partial Q_2 \partial Q_1} & \frac{\partial^2 \bar{D}''}{\partial Q_2^2} & \cdots & \frac{\partial^2 \bar{D}''}{\partial Q_2 \partial Q_m} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 \bar{D}''}{\partial Q_m \partial Q_1} & \frac{\partial^2 \bar{D}''}{\partial Q_m \partial Q_2} & \cdots & \frac{\partial^2 \bar{D}''}{\partial Q_m^2} \end{array} \right]$$

(D-1)

The entries in the above matrix are given by $\partial^4 \bar{D}''/\partial Q_i^4 \partial Q_j^4$ (see Eqs. B-3 and B-4). Note that $\partial^4 \bar{D}''/\partial Q_i^4 \partial Q_j^2 = 0$. The PR-EOS can be used to calculate these entries.
The matrix $H''$ is defined as

$$
\begin{align}
H'' &= 
\begin{bmatrix}
\frac{\partial^2 D_{12}}{\partial Q_1^2} & \frac{\partial^2 D_{12}}{\partial Q_1 \partial Q_2} & \cdots & \frac{\partial^2 D_{12}}{\partial Q_1 \partial Q_m} \\
\frac{\partial^2 D_{12}}{\partial Q_2 \partial Q_1} & \frac{\partial^2 D_{12}}{\partial Q_2^2} & \cdots & \frac{\partial^2 D_{12}}{\partial Q_2 \partial Q_m} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial^2 D_{12}}{\partial Q_m \partial Q_1} & \frac{\partial^2 D_{12}}{\partial Q_m \partial Q_2} & \cdots & \frac{\partial^2 D_{12}}{\partial Q_m^2}
\end{bmatrix}
\end{align}
$$

We take the derivative of Eq. 25 with respect to $y_j$ ($j = 1, \ldots, c-1$), and define $C_{y j}$ as

$$
C_{y j} = \frac{\partial Q_j^a}{\partial y_j} = q_{y j} - q_{y c} \quad \alpha = 1, \ldots, M; j = 1, \ldots, c - 1.
$$

Let us define matrix $C$ with elements $C_{y j}$. The matrix $C''$ has elements $rac{\partial (n(K/K_i))}{\partial y_k}$ from Eq. C-1.

We take the derivatives of $D''$ with respect to $y_j$ and $y_c$, and define $U_{y j}$ as

$$
U_{y j} = \frac{\partial D''}{\partial y_j} = \frac{\partial \ln(K/K_i)}{\partial y_k} = \frac{\delta_{y j} + 1}{y_k - y_c} \quad j, k = 1, \ldots, c - 1.
$$

Next, we define the matrix $U$ with elements $U_{y j}$. One can show that the elements of $U^{-1}$ are given by

$$
[U]^{-1}_{y j} = \frac{y_j - y_c}{y_j - y_c}.
$$

From Eq. 38, one obtains

$$
[H'']^{-1} = \frac{\partial Q_j^a}{\partial y_k} = \frac{\partial \ln K}{\partial y_k} \cdot \frac{\partial \ln K}{\partial \beta} = C U^{-1} C', \quad \text{.............. (D-6)}
$$

where $\ln K = (\ln K_1/K_1, \ln K_2/K_1, \ldots, \ln K_c/K_1)$.

Combining Eqs. D-5 and D-6 provides the elements of $[H'']^{-1}$ given by

$$
[H'']^{-1} = \frac{\partial Q_j^a}{\partial \beta} = \sum_{i=1}^{c-1} y_i C_{y i} \left( C_i - \sum_{p=1}^{c-1} C_{y p} Q_p \right)
$$

$$
j, k = 1, \ldots, M. \quad \text{.............. (D-7)}
$$

The matrix $[H'']^{-1}$ is symmetric.

Finally, the expression for the gradient vector is given by

$$
\left( \frac{\partial V}{\partial Q} \right) = \beta + \frac{\partial V}{\partial Q_i} \cdot \frac{\partial V}{\partial Q_j} \quad \alpha = 1, \ldots, M. \quad \text{.............. (D-8)}
$$

Eq. 32 is used in the derivation of the above equation. As was pointed out earlier, the second derivative $(\frac{\partial^2 V}{\partial Q_i \partial Q_j}) = 0$ (see Eq. B-6).

All the derivations in the paper are based on stability testing of liquid phase by examination of the trial gas phase. Similar derivations for the stability testing of gas phase are obtained by following our procedure.

### SI Metric Conversion Factors

| bar $\times 1.0^*$ | E+05 $= \text{Pa}$ |
---|---|

Abbas Firoozabadi is a senior scientist and director at the Reservoir Engineering Research Inst. (REE) in Palo Alto, California, and a Professor at Imperial College London. e-mail: af@reerin.org. His main research activities center on thermodynamics of hydrocarbon reservoirs and production and on multiphase-multicomponent flow in fractured petroleum reservoirs. Firoozabadi holds a BS degree from Abadan Inst. of Technology, Abadan, Iran, and MS and PhD degrees from the Illinois Inst. of Technology, Chicago, all in gas engineering. Firoozabadi is the recipient of the 2002 SPE Anthony Lucas Gold Medal. Huanquan Pan is a software developer at IonCircle Genomics in Palo Alto, California. Previously, he was a scientist with the Reservoir Engineering Research Inst., where he worked on the modeling of asphaltene and wax precipitation and the development of efficient phase-equilibrium algorithms for compositional reservoir simulation. Pan holds a PhD degree in chemical engineering from Zhenjiang U. in Hangzhou, China.