

# Critical Point and Saturation Pressure Calculations for Multipoint Systems

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## Abstract

Calculation of fluid properties and phase equilibria is important as a general reservoir engineering tool and for simulation of the carbon dioxide or rich gas multiple-contact-miscibility (MCM) mechanisms. Of particular interest in such simulations is the near-critical region, through which the compositional path must go in an MCM process.

This paper describes two mathematical techniques that enhance the utility of an equation of state for phase equilibrium calculations. The first is an improved method of estimating starting parameters (pressure and phase compositions) for the iterative saturation pressure (bubble-point or dew-point) solution of the equation of state. Techniques previously have been presented for carrying out this iterative solution; however, the previously described procedure for obtaining initial parameter values was not satisfactory in all cases. The improved method utilizes the equation of state to estimate the parameter values. Since the same equation then is used to calculate the saturation pressure, the method is self-consistent and results in improved reliability.

The second development is the use of the equation of state to calculate directly the critical point of a fluid mixture, based on the rigorous thermodynamic criteria set forth by Gibbs.<sup>1</sup> The paper presents an iterative method for solving the highly nonlinear equations. Methods of obtaining initial estimates of the critical temperature and pressure also are presented.

The techniques described are illustrated with reference to a modified version of the Redlich-Kwong equation of state (R-K EOS); however, they are applicable to other equations of state. They have been used successfully for a wide variety of reservoir

fluid systems, from a simple binary to complex reservoir oils.

## Introduction

MCM processes such as CO<sub>2</sub> or rich gas miscible displacements (conducted at pressures below the contact-miscible pressure) traverse a compositional path that goes through the near-critical region. This has been described in several papers.<sup>2-4</sup> Simulation of an MCM process requires the use of an equation of state to describe the liquid- and vapor-phase saturations and compositions. Fussell and Yanosik<sup>5</sup> described an MVNR (minimum-variable Newton-Raphson) method for solution of a version of the R-K EOS. They discussed some of the difficulties of obtaining solutions to the equation of state in the near-critical region and showed that the MVNR method gave improved results.

Experience with the MVNR method has demonstrated a need for an improved estimate of initial iteration parameters (pressure, phase compositions) for an iterative solution of saturation (dew-point and bubble-point) pressures. It was learned that the semitheoretical *K*-value correlation used for initial estimates usually gave satisfactory results when the fluid system contained significant amounts of heavy components (C<sub>7+</sub>) but was often unsatisfactory for fluid systems containing only light components. This type of system is exemplified by the fluids in a dry gas-rich gas mixing zone or by mixtures rich in CH<sub>4</sub>, CO<sub>2</sub>, or N<sub>2</sub>.

Experience also has demonstrated a need for direct calculation of the critical point. While the MVNR solution technique discussed by Fussell and Yanosik<sup>5</sup> exhibits improved convergence in the near-critical region, it often is difficult to obtain converged solutions of the equation of state at compositions within a few percent of the critical composition.

Direct calculation of the critical point (pressure, temperature, and composition) of a mixture would provide a much firmer foundation for estimating initial values of the MVNR iteration variables in this region.

This paper describes, in two sections, the development of (1) an improved technique for estimating starting parameters for saturation pressure calculations using the MVNR solution of the R-K EOS, and (2) a direct critical point solution of the R-K EOS.

## Starting Estimates for Saturation Pressure Calculations

The saturation pressure of a single-phase fluid of fixed composition and fixed temperature is defined as that pressure at which a second phase begins to form. If the fluid initially is a vapor, the pressure at which a liquid phase (in equilibrium with the vapor) begins to form is called a dew-point pressure. If the fluid initially is a liquid, the pressure at which an equilibrium vapor forms is called a bubble-point pressure.

Similar conditions also can exist when a second liquid phase forms from an initially all-liquid fluid or when two phases are present and a third phase begins to form. This section will be concerned only with two-phase (liquid/vapor or liquid/liquid) saturation pressures.

The MVNR procedure<sup>5</sup> for calculating saturation pressures using the R-K EOS requires initial estimates of the saturation pressure and either liquid- or vapor-phase compositions. For a bubble point, the liquid composition is the same as the overall mixture composition, and for a dew point the vapor-phase composition is the overall composition. The problem arises in estimating the unknown composition of the other phase – i.e., the first bubble of vapor formed (for a bubble point) or the first drop of liquid (for a dew point).

The technique described by Fussell and Yanosik<sup>5</sup> and by Peng and Robinson<sup>6</sup> used a semitheoretical *K*-value correlation to obtain initial estimates of phase compositions. This approach was found inadequate for estimating compositions for systems such as dry gas-rich gas mixtures and some CO<sub>2</sub>/oil mixtures. Additionally, the correlation cannot be used to obtain all the *K*-values required for more complex CO<sub>2</sub>/hydrocarbon systems, such as those in which three or more phases form.<sup>7</sup> For these reasons, it is desirable to employ a more self-consistent method of estimating starting values of the iteration parameters.

## Description of Method

The approach taken to obtain an improved method was to use the equation of state to obtain both the initial estimates of saturation pressure and phase composition and the final converged solution.

The method is based on approximation of the phase compositions at progressively higher pressures until a pressure region is reached in which the saturation pressure conditions are satisfied. This

pressure and the corresponding phase compositions then are used to begin the MVNR solution. The key to the success of the method is a phase composition correction applied at each iteration, described as follows.

The basis of a phase equilibrium calculation is equality of the component fugacities in the coexisting phases:

$$f_{iL} = f_{iV}; 1 \leq i \leq n, \dots \dots \dots (1)$$

where

$$f_{iL} = x_i p \Psi_{iL}; 1 \leq i \leq n, \dots \dots \dots (2)$$

and

$$f_{iV} = y_i p \Psi_{iV}; 1 \leq i \leq n, \dots \dots \dots (3)$$

The fugacity coefficients,  $\Psi_{iL}$  and  $\Psi_{iV}$ , expressed in terms of the R-K EOS are presented in Appendix A. These coefficients are composition-, temperature-, and pressure-dependent.

For a saturation pressure calculation the composition of one phase (liquid, for a bubble point; vapor, for a dew point) is known. Thus, for a bubble point the  $x_i$ 's are known, and the vapor phase composition is given by

$$\begin{aligned} y_i &= (p \Psi_{iL} x_i) / (p \Psi_{iV}) \\ &= x_i (\Psi_{iL} / \Psi_{iV}); 1 \leq i \leq n, \dots \dots \dots (4) \end{aligned}$$

For a dew point the  $y_i$ 's are known, and the liquid phase composition is given by

$$\begin{aligned} x_i &= (p \Psi_{iV} y_i) / (p \Psi_{iL}) \\ &= y_i (\Psi_{iV} / \Psi_{iL}); 1 \leq i \leq n, \dots \dots \dots (5) \end{aligned}$$

Initially, both the pressure (and, thus, the component fugacity coefficients) and the second phase composition are unknown. The estimation method involves the following steps.

1. Choose a (low) starting pressure – e.g., 1 psi.
2. Calculate  $\Psi_{iL}$  and  $\Psi_{iV}$  at the assumed pressure, using compositions determined in the previous iteration. For the first iteration an approximation of  $\Psi_{iL}$  or  $\Psi_{iV}$  (for a dew point or bubble point, respectively) must be used. Suitable approximations are discussed later.
3. Calculate the composition of the unknown phase:

$$y_i = x_i (\Psi_{iL} / \Psi_{iV}); 1 \leq i \leq n$$

for a bubble point, or for a dew point.

$$x_i = y_i (\Psi_{iV} / \Psi_{iL}); 1 \leq i \leq n.$$

If the sum of the calculated phase compositions is less than 1, the assumed pressure is greater than the saturation pressure. If the sum is greater than 1, the assumed pressure is too low.<sup>8</sup>

4. Correct the pressure estimate in the direction indicated by Step 3. A correction of 100 to 300 psi (700 to 2,100 kPa) has been found to be satisfactory

for each iteration until the saturation pressure is exceeded. Thereafter, the half-interval method may be used to narrow the search range.

5. Correct the unknown phase composition ( $x$ 's or  $y$ 's) by normalizing. Return to Step 2 and use this composition to recompute the fugacity coefficients at the new estimated pressure.

This successive substitution method, in principle, could be used to determine the saturation pressure to any desired accuracy. However, as Fussell and Yanosik<sup>5</sup> have shown, the MVNR method generally results in more rapid convergence once the region of the saturation pressure is estimated reasonably well. Thus, the iteration (Steps 1 through 5) is halted when the saturation pressure is localized within a reasonable range – e.g.,  $\pm 20$  psi ( $\pm 140$  kPa). The resulting phase compositions and pressure then are used as initial estimates for the MVNR solution.

As mentioned in Step 2, an estimate of  $\Psi_{iL}$  and  $\Psi_{iV}$  must be made for the first iteration.  $\Psi_{iV} = 1$  is a satisfactory approximation (at low pressure) for a bubble-point calculation. For a dew point,  $\Psi_{iL}$  may be estimated as

$$\Psi_{iL} = \Psi_i^0 \exp[(Z_L^0(p/p_{si} - 1))], \quad 1 \leq i \leq n, \dots \dots \dots (6)$$

where  $\Psi_i^0$  is the pure component fugacity coefficient evaluated at the pure component vapor pressure,  $p_{si}$ . The vapor pressure may be estimated from the Clausius-Clapeyron equation<sup>9</sup> as

$$p_{si} = p_{ci} \exp\left[\left(\frac{\Delta H_{vi}}{T_{ci}}\right)\left(1 - \frac{T_{ci}}{T}\right)\right] \dots \dots \dots (7)$$

One precaution is necessary for a bubble-point solution: the initial pressure estimate must be within the range where one of the three possible solutions of the equation of state for the liquid-phase compressibility is “liquid-like.” It is necessary, then, at the first entrance to Step 2 to calculate liquid-phase compressibilities at increasing pressures until either: (1) the liquid-phase compressibility is less than one-third (pure-component critical compressibility) or (2) the liquid-phase compressibility reaches a minimum, then increases with increasing pressure. The approximate pressure at which this minimum occurs is used as the initial pressure for the iteration.

The procedure described above for dew points also may be used to find lower dew points (below which only vapor exists). The only modification required is in Step 4, where

$$\sum_{i=1}^n x_i < 1$$

indicates the pressure is *less than* the lower dew-point pressure, and

$$\sum_{i=1}^n x_i > 1$$

indicates the estimated pressure is *too high*.

A variation of this technique is applicable to estimation of phase compositions for a flash calculation in the two-phase region. In this variation,

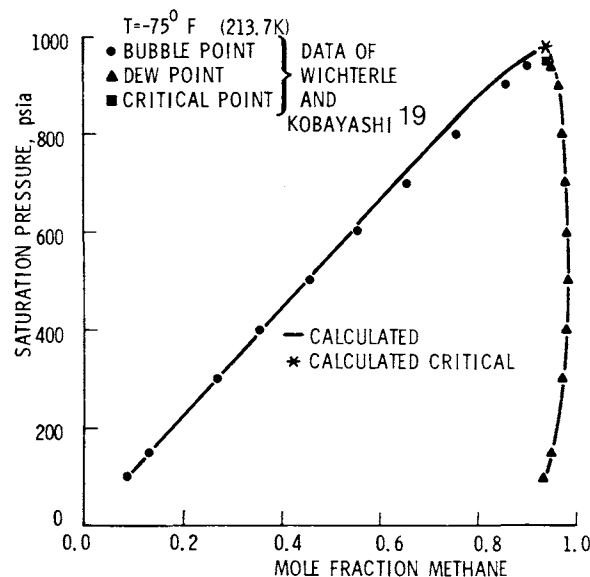


Fig. 1 – Pressure/composition diagram for the methane/propane system.

$K$ -values ( $y_i/x_i$ ) are calculated at Step 5 of the procedure. The mixture composition  $z_i$  then is flashed, using these  $K$ -values, to obtain improved estimates of both  $x_i$  and  $y_i$ . These compositions are used in Step 2 to calculate fugacity coefficients for the next higher pressure. The iteration is halted when the desired flash pressure is reached, and the phase compositions are used as estimates for the MVNR solution.

Since the procedures described above use only the equation of state for iteration, the fugacity coefficients are valid for any two-phase region, whether liquid/liquid or liquid/vapor. In addition, since the estimated pressure and phase compositions are obtained using the equation of state that also is used to calculate the final solution, fewer MVNR iterations should be required.

The method requires somewhat more computer time to obtain initial estimates of phase compositions than does the  $K$ -value correlation used by Fussell and Yanosik<sup>5</sup> and by Peng and Robinson.<sup>6</sup> However, fewer MVNR iterations usually are required for convergence. The net result is a faster and, most important, more reliable calculation technique.

Examples of the application of this method are described in the section “Examples of Calculated Phase Envelopes.”

## Critical Point Calculations

### Statement of Problem

The critical point of a fluid is the temperature, pressure, and composition at which the liquid and vapor phases become indistinguishable. The density, refractive index, and all other properties of the two phases approach the same values. For a pure component, this occurs at a fixed temperature and pressure. For a fluid system, critical points may exist over a range of temperature, pressure, and compositions; however, each fixed composition has a

corresponding fixed critical temperature and pressure. This critical point occurs at the junction of the bubble-point and dew-point pressure curves, as shown in Fig. 1 for the methane/propane binary.

Knowledge of the location of the critical point and an ability to calculate fluid properties in the near-critical region are important because the compositional path for an MCM process must pass through this region.

Spencer *et al.*<sup>10</sup> discuss several empirical methods that have been proposed to estimate critical points of multicomponent mixtures. While these methods are relatively simple, they share the disadvantage that the calculated critical point may not be consistent with bubble points and dew points calculated using an equation of state. It would be highly desirable to use the same equation of state for both saturation pressure calculations and the critical point calculation, thus guaranteeing consistency.

### Thermodynamic Theory

Gibbs,<sup>1</sup> over 100 years ago, set forth the criteria that an equation of state must satisfy at the critical point. More recently, Modell<sup>11</sup> and Reid and Beegle<sup>12</sup> have discussed alternative forms of the criteria, showing that there are many different but equivalent forms. In particular, the criteria may be based on either the Gibbs free energy or the Helmholtz free energy. Reid and Beegle<sup>12</sup> note that there is a reduction in the complexity of the equations if they are based on the Helmholtz free energy. Several researchers<sup>13-15</sup> have used the criteria to find critical points of binary mixtures, and Peng and Robinson<sup>16</sup> extended the work to multicomponent mixtures. The latter used the Peng-Robinson equation of state and the critical criteria based on the Gibbs free energy.

The form of the critical criteria to be used in this paper is that based on the Helmholtz free energy, which can be expressed mathematically as

$$A = \int_V^\infty \left( p - \frac{NRT}{V} \right) dV - RT \sum_{i=1}^n N_i \ln \left( \frac{V}{N_i RT} \right) + \sum_{i=1}^n N_i (U_i^0 - TS_i^0) \dots \dots \dots (8)$$

This equation is written with extensive variables (variables dependent on the mass present in the system, such as mole numbers  $N_i$  for each component  $i$  and system volume  $V$ ). For the present purpose this is more convenient than the equivalent form of the equation expressed in intensive (mass-independent) variables. Derivatives of the Helmholtz free energy,  $A$ , will be denoted by a subscript (e.g.,  $A_V$ ,  $A_{N_i}$ ) indicating the differentiation variable (volume  $V$  or mole number  $N_i$  of component  $i$ ).

Briefly, the criteria that must be satisfied at a critical point are that two determinants  $D$  and  $D^*$  be equal to zero:

$$D = \begin{vmatrix} A_{VV} & A_{N_1V} & A_{N_2V} & \dots & A_{N_{n-1}V} \\ A_{N_1V} & A_{N_1N_1} & A_{N_2N_1} & \dots & A_{N_{n-1}N_1} \\ A_{N_2V} & A_{N_1N_2} & A_{N_2N_2} & \dots & \dots \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ A_{N_{n-1}V} & A_{N_1N_{n-1}} & \dots & A_{N_{n-1}N_{n-1}} \end{vmatrix} = 0, \dots \dots \dots (9)$$

$$D^* = \begin{vmatrix} A_{VV} & A_{N_1V} & \dots & A_{N_{n-1}V} \\ A_{N_1V} & A_{N_1N_1} & \dots & A_{N_{n-1}N_1} \\ \vdots & \vdots & \ddots & \vdots \\ A_{N_{n-2}V} & A_{N_1N_{n-2}} & \dots & A_{N_{n-1}N_{n-2}} \\ D_V & D_{N_1} & \dots & D_{N_{n-1}} \end{vmatrix} = 0. \dots \dots \dots (10)$$

$D_V$  and  $D_{N_i}$  are the derivatives of the determinant  $D$  with respect to  $V$  and  $N_i$ , respectively. It should be noted that all composition derivatives are performed while holding the total number of moles constant. This is in contrast to the approach of Reid and Beegle,<sup>12</sup> who state that when mole numbers (extensive properties) are used, only the mole numbers not used in the differentiation (rather than the total number of moles) are held constant. It can be shown that these two approaches are equivalent in the context of Eqs. 9 and 10. The determinants  $D$  and  $D^*$  are completely general; one need only find the Helmholtz free energy,  $A$ , in terms of the particular equation of state to be used, then perform the indicated differentiation.

### Application of Theory Using R-K EOS

The R-K EOS in extensive form is<sup>17</sup>

$$p = \frac{NRT}{V - NB} - \frac{AN^2}{T^{1/2} V(V + NB)} \dots \dots \dots (11)$$

Insertion of the equation of state into Eq. 8 leads to an expression for the Helmholtz free energy:

$$A = NRT \ln \left( \frac{V}{V - BN} \right) + \frac{AN^2}{NBT^{1/2}} \ln \left( \frac{V}{V + BN} \right) - RT \sum_{i=1}^n N_i \ln \left( \frac{V}{N_i RT} \right) + \sum_{i=1}^n N_i (U_i^0 - TS_i^0). \dots \dots \dots (12)$$

Details of the differentiation of Eq. 12 with respect to volume and composition, to obtain the elements of determinants  $D$  and  $D^*$ , are given in Appendix A.

It was found that the values of the determinants,  $D$  and  $D^*$ , in the form of Eqs. 9 and 10 could easily approach  $10^{\pm 80}$  for even a small number of components (e.g.,  $n = 10$ ). For this reason it was necessary to scale the determinant elements to a

reasonable size. This could be done easily since each element is composed of an "ideal term" and terms to correct for nonideality. For example, the  $A_{VV}$  element is given by

$$A_{VV} = \frac{NRT}{(V-BN)^2} + \frac{AN^2}{NBT^{1/2}} \left[ \frac{1}{(V+BN)^2} - \frac{1}{V^2} \right] \dots \dots \dots (13)$$

The "ideal" term is  $NRT/V^2$ . Division of  $A_{VV}$  by  $RT/V^2$  gives a "normalized" value of  $A_{VV}$  near unity (for  $N \approx 1$ ).

Similar scale factors, shown in Appendix A, were derived for the other determinant elements. These scale factors form a consistent set; in evaluating the determinant, each combination of factors is multiplied by the same product of scale factors.

The method of calculating the values of determinants  $D$  and  $D^*$  is described in Appendix B. Several techniques, including the ordering of the determinant rows and the method of calculating derivatives of a determinant, were developed to optimize computational speed and minimize computer storage requirements. These also are presented in Appendix B.

#### Description of Critical Point Solution

As stated above, the determinants  $D$  and  $D^*$  must be zero at a critical point. Given a method of evaluating the determinants, the problem remains of finding the right combination of temperature, pressure, and composition to make these determinants zero.

Eqs. 9 and 10, which describe the critical conditions, are highly nonlinear. Thus, they cannot be solved directly for temperature, pressure, and composition. An iterative technique is required in which one of the variables (temperature, pressure, or composition) is fixed and the other two are varied to obtain values at which Eqs. 9 and 10 are satisfied. A Newton-Raphson technique (using numerical differentiation of  $D$  and  $D^*$  with respect to the iteration variables) and Powell's method<sup>18</sup> have been tried as solution methods and both worked well. The Newton-Raphson method usually gives faster convergence when the initial estimates of the iteration parameters are far from the final solution.

#### Estimation of Critical Point Iteration Parameters

To calculate a critical point using the procedure described above, it is necessary to obtain initial estimates of two of the three parameters (critical temperature, critical pressure, and critical composition). As pointed out by Spencer *et al.*<sup>10</sup> correlations for predicting critical temperature usually are more accurate than those for predicting critical pressure; this was found to be especially true for mixtures of  $\text{CO}_2$  and hydrocarbons. For this reason a technique was developed using a simple molar average of the component critical temperatures as the initial estimate of the mixture critical temperature:

TABLE 1 — HYDROCARBON COMPOSITIONS OF SYNTHETIC OIL AND SACROC OIL (mole fraction)

Component	Synthetic Oil <sup>20</sup>	SACROC Oil <sup>21</sup>
C <sub>1</sub>	0.3332	0.3100
C <sub>2</sub>	0.0310	0.1041
C <sub>3</sub>	0.0405	0.1187
C <sub>4</sub>	0.0596	0.0732
C <sub>5</sub>	0.0408	0.0441
C <sub>6</sub>	0.0308	0.0255
*C <sub>7+</sub>		0.3244
C <sub>7</sub>	0.0500	
C <sub>8</sub>	0.0500	
C <sub>10</sub>	0.3108	
C <sub>14</sub>	0.0533	

\*C<sub>7+</sub> fraction divided into 33 pseudocomponents with molecular weights ranging from 100 to 549, in exponentially decreasing concentration; distribution and component properties chosen to match experimental C<sub>7+</sub> mol wt and density and bubble point of  $\text{CO}_2$ -free oil.

$$T_c = \sum_{i=1}^n z_i T_{ci} \dots \dots \dots (14)$$

The critical pressure estimate then is based on this temperature estimate, described as follows. It is necessary to estimate the critical composition (if it is not fixed) before making the temperature estimate. No general rules have been developed for the composition estimate.

None of the simple critical pressure correlations investigated were found to be satisfactory. However, it is possible, with only slightly more calculation effort, to use the equation of state to estimate the critical pressure. First, it is necessary to estimate the critical temperature (if the composition is fixed) or the composition (if the temperature is fixed). The method described in the first section of the paper then is used to estimate the mixture bubble point or dew point at the specified composition and temperature. Since the critical pressure must lie on the saturation pressure curve, this results in a self-consistent and usually reasonable estimate of the critical pressure. If the estimated composition is near the true critical composition (for fixed temperature), either the bubble-point or dew-point estimate should be satisfactory for this purpose. Our computer program requires that the user specify whether a bubble-point or a dew-point approximation is to be used. However, if a satisfactory approximation to the specified condition is not found, the program searches for an estimate of the alternate condition.

#### Examples of Calculated Phase Envelopes

Phase envelopes (saturation pressure curves and critical points as a function of mixture composition) are presented in Figs. 1 through 3. Fig. 1 shows the saturation pressure curve for the methane/propane binary at  $-75^\circ\text{F}$  (213.7 K) as calculated by the R-K EOS, along with experimental data.<sup>19</sup> The R-K fits this system well; the calculated critical composition is within 0.8 mol% of the experimental critical composition, and the calculated critical pressure is within 35 psi (241 kPa) or 3.6% of the measured critical pressure. Figs. 2 and 3 show phase envelopes for  $\text{CO}_2$ /oil mixtures. Hydrocarbon compositions of the oil mixtures used (a synthetic "crude" oil<sup>20</sup> in Fig. 2

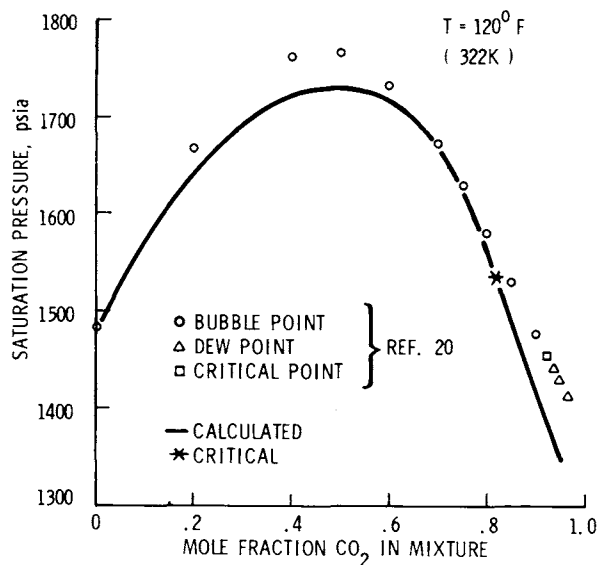


Fig. 2 — Pressure/composition diagram for CO<sub>2</sub>/synthetic oil system.

and SACROC oil<sup>21</sup> in Fig. 3) are shown in Table 1. The C<sub>7</sub><sup>+</sup> fraction of the SACROC oil was divided into 33 pseudocomponents with molecular weights ranging from 100 to 549, in exponentially decreasing concentration with increasing molecular weight. The component distribution and component properties were chosen to match the experimental C<sub>7</sub><sup>+</sup> molecular weight and density and the bubble point of the CO<sub>2</sub>-free oil.

The calculated phase envelopes presented in Figs. 2 and 3 show good agreement with the experimental data. In particular, the shapes of the phase envelopes are described well by the model for these widely differing systems. The fit of the bubble-point or dew-point curve could be improved by a different choice of component interaction parameters ( $C_{ij}$  in Eq. A-3). However, because of the limitations inherent in a cubic equation of state like the R-K, a better fit of a portion of the saturation pressure curve would lead to a poorer fit in some other portion.<sup>22</sup> The calculated critical point of the CO<sub>2</sub>/synthetic oil system (Fig. 2) is about 83 psi (572 kPa) or 6% higher than the experimental critical and 10 mol% lower in CO<sub>2</sub> concentration than the experimental critical. The calculated critical point of the CO<sub>2</sub>/SACROC oil system is about 270 psi (1862 kPa) or 10% higher and 1 mol% higher in CO<sub>2</sub> concentration than indicated by the experimental data.

#### Considerations in the Calculation of a Critical Point

Calculation of a critical point may not be as straightforward as shown in these examples. In the case of a pressure/composition search at fixed temperature, it may be that no critical point exists at the specified temperature. That is, the temperature

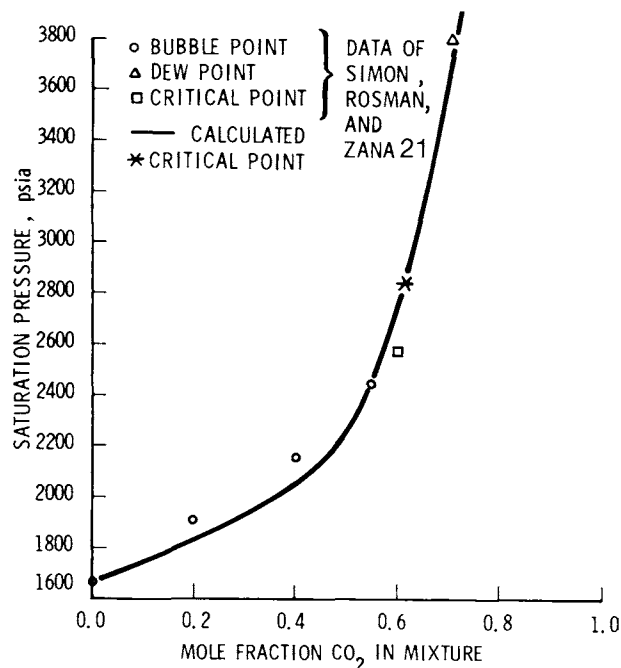


Fig. 3 — Pressure/composition diagram for CO<sub>2</sub>/SACROC oil system.

chosen may be above the critical temperature for the entire range of allowable compositions. When the composition is specified and the pressure/temperature space is searched, it also is possible that no critical point exists. An example is the CO<sub>2</sub>/C<sub>14</sub> system, for which there is a composition region in which there is no criticality.<sup>23</sup> This is particularly true with mixtures that may exhibit more than two phases (such as liquid/liquid/vapor, solid/liquid/liquid, etc.). Normally, the absence of a critical point will be evident when the computations do not show convergence (which should be quadratic in the near-critical region). In these cases it may be necessary to investigate a portion or all of the saturation pressure diagram to find whether a critical point can exist under the conditions specified.

The computer time required for solution of a critical point problem increases exponentially with the number of components in the fluid. For example, the CPU time required to calculate  $D$  and  $D^*$  values for 2, 11, and 40 components was 0.2, 0.98, and 21.3 seconds, respectively, on an IBM 370/158 computer. For 20 components, about 40% of this time is spent in calculating the derivative of determinant  $D$  with respect to the component mole fractions ( $D_{N_i}$  in Eq. 10).

#### Summary

A method has been developed for predicting critical points of multicomponent mixtures using the Redlich-Kwong equation of state (R-K EOS). This is very useful in the simulation of multiple-contact-miscibility (MCM) processes such as CO<sub>2</sub> or rich gas miscible displacement in which the compositional path must pass through the near-critical region.

An improved technique also has been developed

for estimating initial parameters for an iterative saturation pressure solution of the R-K EOS. The success of the iterative process, described in a previous paper<sup>5</sup> on MVNR (minimum-variable Newton-Raphson) methods, is highly dependent on these initial estimates. The new technique does not rely on empirical correlations and has proved satisfactory in all cases tried to date.

These techniques, while illustrated with reference to a particular equation of state, also are applicable to any other equation of state. The techniques greatly enhance the utility of an equation of state in simulation of MCM processes.

## Nomenclature

- $a$  = temperature, pressure, and composition dependent component parameter  
 $A$  = temperature, pressure, and composition dependent phase parameter  
 $b$  = temperature, pressure, and composition dependent component parameter  
 $B$  = temperature, pressure, and composition dependent phase parameter  
 $C_{ij}$  = interaction parameter for component  $i$  with component  $j$   
 $d$  = element of adjoint matrix  
 $D, D^*$  = determinants  
 $f$  = fugacity  
 $\Delta H_v$  = heat of vaporization  
 $K$  = equilibrium ratio,  $K_i = y_i/x_i$   
 $M_{N_i}$  = derivative of array  $M$  by  $N_i$   
 $M_V$  = derivative of array  $M$  by  $V$   
 $n$  = number of components  
 $N$  = total number of moles  
 $N_i$  = number of moles of component  $i$   
 $p$  = pressure  
 $R$  = universal gas constant  
 $S_i^0$  = standard state molar entropy of component  $i$   
 $T$  = temperature  
 $u_i$  = exponent in Eq. A-15,  $A_L(2a_{iL} - b_{iL})/B_L$   
 $U_i^0$  = standard state molar internal energy of component  $i$   
 $V$  = volume  
 $w_i$  = exponent in Eq. A-16,  $A_V(2a_{iV} - b_{iV})/B_V$   
 $x_i$  = mole fraction of component  $i$  in the liquid phase  
 $y_i$  = mole fraction of component  $i$  in the vapor phase  
 $z_i$  = mole fraction of component  $i$  in the fluid  
 $Z$  = phase compressibility factor  
 $Z^0$  = phase compressibility factor of pure component  
 $\alpha_{ij}$  = temperature dependent component parameter

$$\alpha_{ij}'' = 2(\alpha_{ij} - \alpha_{in} - \alpha_{jn} + \alpha_{nn})$$

$$\alpha_{\ell}' = 2 \sum_{i=1}^n N_i (\alpha_{i\ell} - \alpha_{in})$$

$A$  = Helmholtz free energy

$\beta_i$  = temperature dependent component parameter

$$\beta_{\ell}' = \beta_{\ell} - \beta_n$$

$$\delta_{ij} = \text{Kronecker delta: } \delta_{ij} \begin{cases} 0, & i \neq j \\ 1, & i = j \end{cases}$$

$\Psi_i$  = component fugacity coefficient,  $f_i/(px_i)$

$\Omega_a, \Omega_b$  = generalized component parameters; function of the reduced temperature and component Pitzer acentric factor

## Subscripts

- $c$  = critical  
 $i, j, k$  = component number  
 $L$  = liquid phase  
 $s$  = saturation  
 $V$  = vapor phase

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## APPENDIX A

### Formulation of the Critical Criteria

At a critical point, the determinants  $D$  and  $D^*$  (Eqs. 9 and 10) must be zero.

The elements of the determinants are derivatives of the Helmholtz free energy with respect to volume  $V$  and mole number  $N_i$ . The elements  $D_v$  and  $D_{N_i}$  of  $D^*$  are derivatives of the determinant  $D$  with respect to  $V$  and  $N_i$ , respectively.

The Helmholtz free energy is given by

$$A = \int_V^\infty \left( p - \frac{NRT}{V} \right) dV - RT \sum_{i=1}^n N_i \ln \left( \frac{V}{N_i RT} \right) + \sum_{i=1}^n N_i (U_i^0 - TS_i^0), \dots \quad (\text{A-1})$$

where  $U_i^0$  is the standard state molar internal energy of component  $i$  and  $S_i^0$  is the standard state molar entropy. The last summation of Eq. A-1 drops out upon differentiation with respect to  $V$  or second differentiation with respect to  $N_i$ . Substitution of the equation of state to be used into Eq. A-1 leads to the expressions required for the determinant elements.

The R-K EOS in extensive form is<sup>17</sup>

$$p = \frac{NRT}{V - NB} - \frac{AN^2}{T^{1/2} V(V + NB)}, \dots \quad (\text{A-2})$$

where  $A$  and  $B$  are defined as

$$\alpha_{ij} = \alpha_{ji} = (1 - C_{ij}) R^2 \left\{ \frac{\Omega_{a_i} T_{c_i}^{2.5}}{p_{c_i}} \cdot \frac{\Omega_{a_j} T_{c_j}^{2.5}}{p_{c_j}} \right\}^{1/2}, \dots \quad (\text{A-3})$$

$$\beta_i = \Omega_{b_i} RT_{c_i} / p_{c_i}, \dots \quad (\text{A-4})$$

$$A = \sum_{i=1}^n \sum_{j=1}^n z_i z_j \alpha_{ij}, \dots \quad (\text{A-5})$$

$$B = \sum_{i=1}^n z_i \beta_i, \dots \quad (\text{A-6})$$

The parameter  $C_{ij}$  is a component interaction parameter and is independent of pressure, temperature, or composition. The values of the component parameters  $\Omega_{a_i}$  and  $\Omega_{b_i}$  are independent of pressure and composition but are dependent on temperature.<sup>17</sup>

Substitution of Eq. A-2 into Eq. A-1 gives (after simplification)

$$A = NRT \ln \left( \frac{V}{V - BN} \right) + \frac{AN^2}{NBT^{1/2}} \ln \left( \frac{V}{V + BN} \right) - RT \sum_{i=1}^n N_i \ln \left( \frac{V}{N_i RT} \right) + \sum_{i=1}^n N_i (U_i^0 - TS_i^0), \dots \quad (\text{A-7})$$

Eq. A-7 then is differentiated with respect to volume and composition to obtain the required determinant elements  $A_{VV}$ ,  $A_{N_i V}$ , and  $A_{N_i N_j}$ .

Determinant  $D^*$  requires, in addition, differentiation of determinant  $D$  with respect to volume and composition. This introduces the variables  $A_{VVN_i}$ ,  $A_{VN_i N_j}$ , and  $A_{N_i N_j N_k}$ .

Thus, evaluation of the determinants  $D$  and  $D^*$  requires only the values of the elements  $A_{VV}$ ,  $A_{VVV}$ ,  $A_{VN_i}$ ,  $A_{VVN_i}$ ,  $A_{VN_i N_j}$ ,  $A_{N_i N_j}$ , and  $A_{N_i N_j N_k}$ , where  $i, j, k$  range from 1 to  $n-1$  and  $n$  is the total number of components. The method of solution of the determinants is given in Appendix B.

The composition derivatives  $A_{N_i V}$ ,  $A_{N_i N_j}$ , etc., are taken with the total number of moles held constant. That is if  $N_i$  varies by an amount  $\delta N$ , then  $N_n$  must vary by the same amount ( $-\delta N$ ).

The derivatives are shown in Table 2.

### Scaling of Determinant Elements

Problems may be encountered in evaluating the determinants  $D$  and  $D^*$  due to the size of the determinant elements. For even moderate numbers of fluid components (e.g., 10), the determinant values (using the elements as defined in the previous section) may approach  $10^{\pm 80}$ . For this reason, it is necessary to scale the determinant elements to a "reasonable" size. The scale factors of Table 3, based on the "ideal" term of each determinant element, have been found to be a consistent and reasonable set.

### Fugacity Coefficients Defined With the R-K Equation of State

Fugacity coefficients  $\Psi_{iL}$  and  $\Psi_{iV}$  are defined in terms of the R-K EOS as<sup>5</sup>

$$\Psi_{iL} = \frac{\exp[b_{iL}(Z_L - 1)]}{(Z_L - B_L)(1 + B_L/Z_L)^{u_i}}, \dots \quad (\text{A-8})$$



$$\Psi_{iV} = \frac{\exp[b_{iV}(Z_L - 1)]}{(Z_V - B_V)(1 + B_V/Z_V)^{w_i}} \dots \dots \dots (\text{A-9})$$

Notation is defined in the Nomenclature.

## APPENDIX B

### Evaluation of Determinants

The determinants  $D$  and  $D^*$  (Eqs. 9 and 10) are easy to evaluate. However, approaching the problem in the most straightforward manner involves a total of  $n^2 + 2$  determinant evaluations, including determinant derivatives, to find the values of  $D$  and  $D^*$ . This requires more computer time than is necessary. The most obvious opportunity for computational savings can be seen by comparison of the forms of  $D$  and  $D^*$ . The row ordering of the arrays has been chosen to show that the arrays are identical, except for the last row. Therefore, if determinant  $D$  is evaluated by computing cofactors of the last row, the

same cofactors may be used to evaluate the determinant  $D^*$ .

A further savings can be realized by in the calculation of the determinant derivatives. Upon inspection it becomes obvious that the derivative of a determinant ( $D$ ) with respect to a variable (e.g.,  $V$ ) is the sum of the element-by-element products of two matrices. One matrix contains the cofactors of the original matrix, while the other contains the derivatives of the original matrix elements with respect to the variable.

Thus, if the matrix  $D$  is (for a three-component system)

$$D = \begin{bmatrix} A_{VV} & A_{N_1V} & A_{N_2V} \\ A_{N_1V} & A_{N_1N_1} & A_{N_2N_1} \\ A_{N_2V} & A_{N_1N_2} & A_{N_2N_2} \end{bmatrix} \dots \dots \dots (\text{B-1})$$

and the adjoint matrix (matrix of cofactors) is

TABLE 2

$$\begin{aligned} A_{VV} &= \frac{NRT}{(V-BN)^2} + \frac{AN^2}{NBT^{1/2}} \left[ \left( \frac{1}{V+BN} \right)^2 - \left( \frac{1}{V} \right)^2 \right] \\ A_{VVV} &= -\frac{2NRT}{(V-BN)^3} + \left( \frac{2AN^2}{NBT^{1/2}} \right) \left[ \left( \frac{1}{V} \right)^3 - \left( \frac{1}{V+BN} \right)^3 \right] \\ A_{N_1V} &= -\frac{NRT\beta_i'}{(V-BN)^2} + \frac{1}{NBT^{1/2}} \left\{ \left[ \frac{1}{V} - \frac{1}{V+BN} \right] \left[ \alpha_i' - \frac{AN^2\beta_i'}{BN} \right] + \frac{AN^2\beta_i'}{(V+BN)^2} \right\} \\ A_{N_1N_1} &= \frac{NRT\beta_i'\beta_j'}{(V-BN)^2} + RT \left[ \frac{\delta_{ij}}{N_j} + \frac{1}{N_n} \right] \\ &\quad + \frac{1}{NBT^{1/2}} \left\{ - \left[ \frac{1}{V+BN} + \frac{1}{BN} \ln \left( \frac{V}{V+BN} \right) \right] \left[ \alpha_i'\beta_j' + \alpha_j'\beta_i' \right] \right. \\ &\quad \left. - \frac{2AN^2\beta_i'\beta_j'}{BN} \right] + \alpha_{ij}'' \ln \left( \frac{V}{V+BN} \right) + \frac{AN^2\beta_i'\beta_j'}{(V+BN)^2} \left\} \\ A_{N_1VV} &= \frac{2NRT\beta_i'}{(V-BN)^3} + \frac{1}{NBT^{1/2}} \left\{ \left[ \alpha_i' - \frac{AN^2\beta_i'}{NB} \right] \left[ \frac{1}{(V+BN)^2} - \frac{1}{V^2} \right] - \frac{2AN^2\beta_i'}{(V+BN)^3} \right\} \\ A_{N_1N_1V} &= -\frac{2NRT\beta_i'\beta_j'}{(V-BN)^3} + \frac{1}{NBT^{1/2}} \left\{ \left[ \frac{1}{BN} \left( \frac{1}{V+BN} - \frac{1}{V} \right) \right. \right. \\ &\quad \left. \left. + \frac{1}{(V+BN)^2} \right] \left[ \alpha_i'\beta_j' + \alpha_j'\beta_i' - \frac{2AN^2\beta_i'\beta_j'}{BN} \right] \right. \\ &\quad \left. + \alpha_{ij}'' \left( \frac{1}{V} - \frac{1}{V+BN} \right) - \frac{2AN^2\beta_i'\beta_j'}{(V+BN)^3} \right\} \\ A_{N_1N_1N_1} &= \frac{2NRT\beta_i'\beta_j'\beta_k'}{(V-BN)^3} + RT \left[ \frac{-\delta_{ijk}}{N_k^2} + \frac{1}{N_n^2} \right] \\ &\quad + \frac{1}{NBT^{1/2}} \left\{ - \left[ \left( \frac{1}{V+BN} \right) + \frac{1}{BN} \ln \left( \frac{V}{V+BN} \right) \right] \left[ \alpha_{ij}''\beta_k' + \alpha_{ik}''\beta_j' \right. \right. \\ &\quad \left. \left. + \alpha_{jk}''\beta_i' \right] + \left[ \left( \frac{1}{V+BN} \right) \left( \frac{2}{BN} + \frac{1}{V+BN} \right) + \frac{2}{(BN)^2} \ln \left( \frac{V}{V+BN} \right) \right] \right. \\ &\quad \left. \cdot \left[ \alpha_i'\beta_j'\beta_k' + \alpha_j'\beta_i'\beta_k' + \alpha_k'\beta_i'\beta_j' \right] \right. \\ &\quad \left. - (AN^2\beta_i'\beta_j'\beta_k') \left[ \left( \frac{1}{V+BN} \right) \left( \frac{6}{(BN)^2} + \frac{2}{(V+BN)^2} + \frac{3}{BN(V+BN)} \right) \right. \right. \\ &\quad \left. \left. + \frac{6}{(BN)^3} \ln \left( \frac{V}{V+BN} \right) \right] \right\} \end{aligned}$$

$$D_{adj} = \begin{bmatrix} d_{VV} & d_{N_1V} & d_{N_2V} \\ d_{N_1V} & d_{N_1N_1} & d_{N_2N_1} \\ d_{N_2V} & d_{N_1N_2} & d_{N_2N_2} \end{bmatrix}, \dots \dots \dots (B-2)$$

then the derivative of the determinant  $D$  with respect to  $V$  is the sum of the element-by-element products of  $D_{adj}$  and the matrix

$$M_V = \begin{bmatrix} A_{VVV} & A_{N_1VV} & A_{N_2VV} \\ A_{N_1VV} & A_{N_1N_1V} & A_{N_2N_1V} \\ A_{N_2VV} & A_{N_2N_1V} & A_{N_2N_2V} \end{bmatrix}, \dots \dots \dots (B-3)$$

or

$$\begin{aligned} D_V = & A_{VVV}d_{VV} + A_{N_1VV}(2d_{N_1V}) \\ & + A_{N_2VV}(2d_{N_2V}) + A_{N_1N_1V}(d_{N_1N_1}) \\ & + A_{N_1N_2V}(2d_{N_2N_1}) + A_{N_2N_2V}(d_{N_2N_2}) . \\ & \dots \dots \dots (B-4) \end{aligned}$$

Note that since the matrix  $D$  is symmetric, the adjoint matrix  $D_{adj}$  also is symmetric (i.e.,  $d_{ij} = d_{ji}$ ). Thus, the combination of factors shown in Eq. B-4 is valid.

Similarly, the derivative of the determinant  $D$  with respect to  $N_i$  is the sum of the element-by-element products of the matrix  $D_{adj}$  and the matrix  $M_{N_i}$ :

$$M_{N_i} = \begin{bmatrix} A_{N_iVV} & A_{N_iN_1V} & \dots & A_{N_iN_{n-1}V} \\ A_{N_iN_1V} & A_{N_iN_1N_1} & \dots & A_{N_iN_1N_{n-1}} \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ A_{N_iN_{n-1}V} & A_{N_iN_{n-1}N_1} & \dots & A_{N_iN_{n-1}N_{n-1}} \end{bmatrix} \dots \dots \dots (B-5)$$

The problem of evaluating determinant  $D^*$  then reduces to the following steps.

1. Calculate the (symmetric) adjoint matrix  $D_{adj}$  corresponding to  $D$ .

2. Multiply and add, element-by-element, the derivatives with respect to  $V$  of the elements of  $D$  (matrix  $M_V$ ) by the corresponding cofactors (elements of  $D_{adj}$ ) to obtain  $D_V$ .

3. Multiply  $D_V$  by the first element of the last row of  $D_{adj}$  (cofactor of  $A_{N_{n-1}V}$  in determinant  $D$ ).

4. Multiply and add, element-by-element, the derivatives with respect to  $N_i$  of the elements of  $D$  (matrix  $M_{N_i}$ ) by the corresponding cofactors in (elements of  $D_{adj}$ ) to obtain  $D_{N_i}$ .

5. Multiply  $D_{N_i}$  by the  $N_{i+1}$  element of the last row of  $D_{adj}$  (cofactor of  $A_{N_{n-1}N_i}$ ) in determinant  $D$ .

TABLE 3

Element	Scale Factor to Multiply Element
$A_{VV}$	$V^2 / (RT N_n)$
$A_{VVV}$	$V^3 / (RT N_n)$
$A_{N_iV}$	$V/RT$
$A_{N_iVV}$	$V^2/RT$
$A_{N_iN_j}$	$N_n/RT$
$A_{N_iN_jV}$	$N_n V/RT$
$A_{N_iN_jN_k}$	$N_n^2/RT$

6. Repeat Steps 4 and 5 for  $n-1$  composition derivatives ( $n$  = number of components).

7. Add the terms obtained in Steps 3 and 5 to obtain the value of the determinant  $D^*$ .

Note that the procedure of differentiating a matrix described above is valid for any matrix, whether symmetric or not. However, the matrix  $D_{adj}$ , which was described as the adjoint matrix, actually is the transpose of the adjoint matrix. In this case, because of symmetry, the adjoint matrix and its transpose are identical.

The procedure described above is a straightforward and simple approach. However, it requires computation and storage of a large  $[(n-1) \times (n-1) \times (n-1)]$  array ( $A_{N_iN_jN_k}$ ). Further savings can be realized by use of the symmetry properties of the array elements:

$$\begin{aligned} A_{N_iN_jN_k} &= A_{N_iN_kN_j} = A_{N_jN_iN_k} = A_{N_jN_kN_i} \\ &= A_{N_kN_iN_j} = A_{N_kN_jN_i} . \end{aligned}$$

Inspection of this array shows that it is necessary to calculate the value of only one-sixth of the array elements (in the limit, for large  $n$ ). Further, each unique value of  $A_{N_iN_jN_k}$  then is multiplied by a maximum of six elements of the adjoint matrix  $D_{adj}$ . Therefore, once the adjoint matrix has been generated, it is a simple matter to calculate a value  $A_{N_iN_jN_k}$ , multiply by the appropriate cofactor pairs (which may be one, two, or three unique elements of  $D_{adj}$ , again using symmetry of  $D_{adj}$ ) and sum. The cofactor pairs for  $A_{N_iN_jN_k}$  include the  $D_{adj}$  elements corresponding to the matrix positions  $(i+1, j+1)$ ,  $(i+1, k+1)$ ,  $(j+1, k+1)$  and cofactors from the last row of  $D_{adj}$  in the matrix positions  $(n, i+1)$ ,  $(n, j+1)$ , and  $(n, k+1)$ . Some of these are redundant and are not included in the summation.

Using this method, only one storage location is required for the  $A_{N_iN_jN_k}$  matrix, which if fully stored would require  $n^3$  storage locations (125,000 for  $n = 50$ ). Calculation and storage of only the unique portion of the array (approximately 20,834 elements for  $n = 50$ ) would also save a significant amount of storage space but would require additional computational time for an index-calculating algorithm.

**SPEJ**

Original manuscript received in Society of Petroleum Engineers office July 24, 1978. Paper accepted for publication July 20, 1979. Revised manuscript received Oct. 15, 1979. Paper (SPE 7478) first presented at the SPE 53rd Annual Fall Technical Conference and Exhibition, held in Houston, Oct. 1-4, 1978.

# Discussion of Critical Point and Saturation Pressure Calculations for Multicomponent Systems

(SPE 8871)

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The following comments pertain to some of the material presented by Baker and Luks in "Critical Point and Saturation Pressure Calculations for Multicomponent Systems" (Feb. 1980 *SPEJ*, Pages 15-24).

Phase equilibrium calculations require the use of initial  $K$ -values to start the calculation procedure. Wilson<sup>1</sup> proposed the following equation for generating the starting  $K$ -values for vapor/liquid equilibrium calculations.

$$K_i = \exp\left\{5.37(1 + \omega_i)\left(1 - \frac{1}{T_{R_i}}\right)\right\} / P_{R_i}, \dots \dots (1)$$

where  $i = 1, 2, \dots, N$ .

This equation can be derived from the assumption that the fluid follows Raoult's law and that the logarithm of the reduced vapor pressure of the component is a linear function of the reciprocal reduced temperature. This equation has been used in the Peng-Robinson program<sup>2</sup> since 1976.

Baker and Luks have claimed that Eq. 1 cannot be used to obtain "all" the  $K$ -values required for systems in which three or more phases exist. However, they did not present an equation or correlation that presumably would be able to meet with this requirement. The fact is that more than one set of  $K$ -values are needed to make phase equilibrium calculations for these kinds of systems. Using a single correlation (or equation) cannot generate all the starting  $K$ -values required. Peng and Robinson<sup>2</sup> successfully used the following equation to generate the starting  $K$ -values for the aqueous liquid phase/vapor phase in the  $L_1L_2V$  equilibrium calculations.

$$K_i = 10^6 \left( \frac{P_{R_i}}{T_{R_i}} \right) \dots \dots \dots (2)$$

Eq. 1 was used for the hydrocarbon liquid phase/vapor phase.

With appropriate considerations, various modifications of Eq. 1 can be used to provide reliable starting  $K$ -values in difficult regions such as the near critical or the retrograde region.

By treating the mixture as a single pseudocomponent, the initial values of pressure or temperature for phase boundary calculations can be generated from Eq. 1.

Basically, the method proposed by Baker and Luks for making phase boundary calculations is similar to that used in the Peng-Robinson program. The only major difference seems to be that Baker and Luks use a low starting pressure, while the Peng-Robinson program has the flexibility of either generating automatically a reasonable approximation or using an externally supplied value for the starting pressure. Furthermore, the Peng-Robinson program also has the ability to determine the saturation temperature at specified pressure.

The application of Gibbs critical criteria to the calculation of the critical points of a multicomponent mixture was first attempted by Peng and Robinson. It was shown that the Peng-Robinson equation of state was capable of generating reliable results for the critical condition. At that time, however, no effort was made to find the most efficient way of evaluating the critical criteria, which are two determinants of order  $n-1$  for an  $n$ -component system.

The elements of the determinants are derivatives of the Gibbs free energy. Equivalent critical criteria can be expressed in terms of two determinants of order  $n$

with elements being the derivatives of the Helmholtz free energy. Baker and Luks examined the mathematical nature of the determinants based on the Helmholtz free energy and proposed a computation procedure to evaluate these determinants. It appears that their procedure also can be applied to the determinants of order  $n-1$  that are based on the Gibbs free energy. This infers that a more economical computation can be achieved by using the Gibbs free energy-based determinants than by using the alternative forms.

Recently Heidemann and Khalil<sup>3</sup> presented new forms of the critical criteria that are based on the expansion of the Helmholtz free energy. Their computation procedure requires, during each iteration, the evaluation of only one determinant, the solution of a set of linear simultaneous equations,

and the evaluation of a triple summation function. It is conceivable that their method is more economical to use than either the method proposed by Baker and Luks and that used by Peng and Robinson.

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**SPEJ**