Computation of Tricritical Points in Ternary Systems

Bruce F. Kohse and Robert A. Heidemann
Dept. of Chemical and Petroleum Engineering, The University of Calgary, Calgary, Alberta, Canada T2N 1N4

At tricritical points, four equations in the thermodynamic variables must be satisfied. Methods of evaluating the functions and solving these four equations have recently been developed (Michelsen and Heidemann, 1988). A modified approach to the evaluation of these functions and a new solution procedure for the calculation of tricritical points in equation of state models are presented here. The new solution procedure is evaluated in comparison to previous ones, and its application is made using the Peng-Robinson and Soave-Redlich-Kwong equations of state. The new procedure proved capable of locating tricritical points in a variety of systems with complex multiphase behavior. These included ternary systems with single tricritical points, systems with an ordinary critical point occurring at the same composition as a tricritical point and systems capable of four-phase equilibria with two tricritical points. Comparisons are made with experimental tricritical data for eight systems. The calculations prove to be highly sensitive to pure component and binary parameters in the equation of state models. Features of phase diagrams for tricritical mixtures are discussed as well as the predictions of tricritical points in several homologous series of ternary systems.

Introduction

At an ordinary critical point, two equilibrium phases become identical. Similarly, the state at which three equilibrium phases become simultaneously identical is a tricritical point. These definitions can be extended to critical points of even higher order, such as tetracritical and pentacritical points, where four and five phases become identical, respectively.

The phase rule for a critical point where n phases are identical may be written (Knobler and Scott, 1984)

$$F = C + 3 - P - n \tag{1}$$

where F is the degrees of freedom, C is the number of components and P is the number of phases. Since $F \geq 0$ and $P \geq n$, the minimum number of components required for an nth order critical point is given by: $C \geq 2n - 3$. For an ordinary critical point ($n = 2$), $C \geq 1$; for a tricritical point ($n = 3$), $C \geq 3$; and for a tetracritical point ($n = 4$), $C \geq 5$.

Tricritical points have been located experimentally in three-component systems with V-L-L equilibrium and in four-component systems with L-L-L equilibrium in the presence of a vapor phase. In ternary systems, the tricritical point has zero degrees of freedom; it exists only at a unique pressure, temperature and composition. In quaternary systems, one variable must be specified in order to define the tricritical point. Experimentally, quaternary systems have been studied either at the vapor pressure of the mixture or at a certain fixed pressure. This allows the determination of a line of tricritical points simply by varying the pressure of the system.

The sources of data on tricritical phenomena and the associated three-phase behavior have been reviewed by a number of authors. Kohse (1989) reviews the available tricritical point data and the experimental techniques used to locate these points. Scott (1982) and Knobler and Scott (1984) present data for ternary and quaternary tricritical mixtures and introduce the thermodynamic models for phase behavior in the tricritical region. Widom and Sundar (1986) discuss theoretical aspects of critical phenomena while Luks (1986) discusses sources of three-phase data for binary and ternary light hydrocarbon mixtures.

Computation of critical and tricritical points

Two classical fluid mixture models have been proposed to

Correspondence concerning this article should be addressed to R. A. Heidemann.

describe the phase behavior of tricritical systems. The "order-parameter" expansion model presented by Griffiths (1974) predicts the correct shape of the three-phase region in the vicinity of the tricritical point, while Fox (1978) defines the global phase diagram for the regular solution model, including the region around a tricritical point. These theories are valuable for analyzing and extrapolating experimental data; however, they cannot be used to predict the location of tricritical points in specific systems. Methods utilizing cubic equations of state have been proposed for this purpose.

The development of equation of state methods for calculating tricritical points began with the development of efficient methods for ordinary critical point calculation. Peng and Robinson (1977) and Baker and Luks (1980) presented techniques for solving the rigorous criteria for a critical point in a multicomponent mixture as presented by Gibbs (1876). Both approaches require the evaluation of a potentially large number of determinants and are, therefore, computationally expensive, particularly for mixtures with many components. Heidemann and Khalil (1980), using criteria formulated in terms of the Helmholtz free energy, presented a secure and efficient algorithm for the critical point calculation that requires evaluation of only one determinant and avoids differentiation of determinants. The algorithm utilizes nested one-dimensional searches for the two independent variables. Michelsen (1982, 1984) presented yet another efficient technique for direct computation of critical points that does not involve the evaluation of any determinants but relies on eigenvalue methods and numerical differentiation to produce the needed higher order derivatives.

The criteria for multicritical points in fluid mixtures and the calculation procedures required to solve them using equations of state were presented by Michelsen and Heidemann (1988). They include development of the tricritical point criteria, in terms of both the Gibbs and Helmholtz free energies, as a set of four nonlinear simultaneous equations. Two of the equations are satisfied at an ordinary critical point, but all four must be satisfied at a tricritical point. Two solution procedures are presented by Michelsen and Heidemann: one involves ordinary critical point calculations nested inside a two-dimensional search loop for two composition variables, and the other treats all four equations in a full four-dimensional Newton-Raphson search.

In this article, a modified formulation of the tricritical point criteria of Michelsen and Heidemann (1988) is used to evaluate the four functions in terms of the equation of state variables. Further, two solution procedures are investigated; a modification of the nested procedure mentioned above and a new procedure developed here. The initiation requirements, convergence characteristics and application of each of the two procedures to critical point and tricritical point calculations are investigated. Comparisons are presented between calculations and experimental data for as many systems as possible. Tricritical points are calculated for a variety of systems including ternary mixtures of hydrocarbons, light gases, alcohols and water. The occurrence of simultaneous critical and tricritical behavior in some of these systems is examined and the phase behavior of the tricritical region is also studied.

Criteria for a Tricritical Point

The criteria for critical points of any order may be derived from the Gibbs test of stability for homogeneous phases. The condition of stability in terms of the Helmholtz free energy was given by Gibbs (1876) as follows: a test phase at conditions (T_0, V_0, n_{1_0}, n_{2_0}, ..., n_{N_0}) with Helmholtz free energy A_0 will be stable if, for every alternate phase at conditions (T_0, V, n_1, n_2, ..., n_N) and Helmholtz free energy A, the following inequality is satisfied by D, the "tangent plane distance function:"

$$D=\left[A-A_0+P_0(V-V_0)-\sum_{i=1}^{N}\mu_{i_0}(n_i-n_{i_0})\right]_{T_0}\geq 0 \tag{2}$$

When dealing with equations of state, it is convenient to write Eq. 2 in the form:

$$F=D/RT=\sum_{i=1}^{N}n_i\ln(f_i/f_i^0)+V(P_0-P)/RT\geq 0 \tag{3}$$

The sign of F will determine the stability of the test phase. If $F>0$ for all phases with the volume and temperature of the test phase (but different mole numbers), the test phase is stable, if $F=0$ for some alternative phase but otherwise is positive, the alternate phase is potentially in equilibrium with the test phase, and if $F<0$ for any alternate phase, the test phase is unstable.

Critical (and multicritical) phases are stable phases at the limit of stability and are found by examining the local behavior of F. Following the approach of Michelsen and Heidemann (1988), one mole of the test phase is considered, with mole fractions z_i. These mole fractions can stand in the place of n_{i_0} in Eq. 2. F is regarded as a function of scaled and translated mole numbers defined by

$$X_i=(n_i-z_i)/z_i^{1/2} \tag{4}$$

The mole numbers are assumed to vary according to

$$X=su+s^2w+s^3q+\ldots \tag{5}$$

where s is a scalar variable. The tangent plane function is expanded in a Taylor series around the test point as follows:

$$F=bs^2+cs^3+ds^4+es^5+fs^6+\ldots\ldots \tag{6}$$

Vectors $\boldsymbol{u}$, $\boldsymbol{w}$, $\boldsymbol{q}$, and so on must be such that F is minimized at each value of the scalar s.

The procedures for determining $\boldsymbol{u}$, $\boldsymbol{w}$, $\boldsymbol{q}$ and the coefficients b, c, d, e, f in Eq. 6 are given in the Appendix. Michelsen and Heidemann (1988) have presented a detailed account of the essential mathematics. There are some differences in detail between their approach and the present one that arise from their emphasis on a different "tangent plane distance" function and from differences in the order the equations are handled.

As was shown by Michelsen and Heidemann (1988), at a tricritical point the minimum expansion in Eq. 6 becomes

$$F=fs^6+\ldots \tag{7}$$

and the four equations for a tricritical point may be written

$$b = c = d = e = 0 \tag{8}$$

For the tricritical point to be stable, it is also necessary to have

$$f > 0 \tag{9}$$

Solution Procedures

To solve the four tricritical condition equations, four independent variables must be chosen. Using the Helmholtz free energy form of the tangent plane stability function, two natural independent variables are temperature and volume. This leaves two independent mole fractions to be used. (It was pointed out in the introduction that tricritical systems must have a minimum of three components.) The solution procedures presented here may be used for mixtures with three or more components. The mole fractions of components 1 and 2 are taken as independent variables, while the mole fraction of component 3 is taken as a dependent variable to maintain $\Sigma z_i = 1$. The mole fractions of any other components in the mixture are kept fixed.

Michelsen and Heidemann (1988) have presented two procedures for the solution of the four nonlinear equations $b = c = d = e = 0$. One method nests a critical temperature and volume calculation (solving $b = c = 0$) at fixed composition inside an outer loop that uses a Newton-Raphson procedure (solving $d = e = 0$) to find the tricritical composition. This method is referred to as the "two-dimensional" or "2-D" routine hereafter. The second method they describe is a full four-dimensional Newton-Raphson search to locate the roots of all four equations simultaneously (4-D routine).

In this work, a variation on the Michelsen and Heidemann (1988) 2-D method is used and is compared with a new technique that nests one of the four equations inside an outer loop in which the remaining three are solved. The new technique shall be referred to as the "3-D" routine.

The Heidemann and Khalil (1980) critical point procedure involves an extremely robust inner iteration solving $b = 0$ (in effect) for the temperature at fixed composition and volume. Both the 2-D and 3-D procedures make use of this robust calculation.

The gradient of function $F(X)$ in Eq. 3, denoted by g, and the Hessian can both be found by analytical differentiation without much effort. (See the Appendix.) The Hessian matrix evaluated at the test point is given the symbol $\boldsymbol{B}$. The Heidemann and Khalil (1980) procedure utilizes that the determinant of $\boldsymbol{B}$ is zero when $b = 0$ and entails solving the following equation for the temperature at a fixed volume and composition:

$$\beta(T) = (T/100)^N \det(\boldsymbol{B}) = 0 \tag{10}$$

The factor $(T/100)^N$ is introduced and the procedure is initiated at a high temperature in order to assure that the procedure converges to a meaningful temperature.

Two-dimensional search routine

The steps of the two-dimensional search algorithm are as follows:

(1) At each trial composition z, the critical temperature and volume are found in a nested procedure. The temperature satisfying $\beta(T) = 0$ is found in an inner loop and coefficient c is evaluated as described in the Appendix. It was found useful to follow Heidemann and Khalil (1980) and to solve $[(v - b_m)/b_m]^2 c(v, T(v)) = 0$ for the volume, since convergence behavior is improved. The volume is found in a one-dimensional Newton-Raphson procedure with numerical differentiation to obtain the necessary volume derivative. Coefficients d and e are then evaluated at the critical temperature and volume. The procedures are described in the Appendix.

(2) The critical temperature and volume calculations and the evaluation of functions d and e are repeated for two perturbed compositions as follows: $(z_1 + \epsilon_1, z_2, z_3 - \epsilon_1, \ldots, z_N)$, and $(z_1, z_2 + \epsilon_2, z_3 - \epsilon_2, \ldots, z_N)$, where $\epsilon_i = z_i \times 10^{-3}$. The values are used to calculate numerical partial derivatives of d and e.

(3) New values of z_1, z_2 (and z_3) are located by a two-dimensional Newton-Raphson iteration.

(4) Steps 1 through 3 are repeated until convergence is obtained, that is, until $d = e = 0$.

(5) Coefficient f is evaluated at the tricritical point.

Three-dimensional search routine

The steps of the three-dimensional search algorithm are as follows:

(1) At a trial composition z and a trial volume v, the temperature corresponding to $\beta = 0$ is found using a single interior loop. The functions c, d and e are then evaluated.

(2) Step 1 is repeated for two perturbed compositions and one perturbed volume as follows: $(v, z_1 + \epsilon_1, z_2, z_3 - \epsilon_1, \ldots, z_N)$, $(v, z_1, z_2 + \epsilon_2, z_2 - \epsilon_2, \ldots, z_N)$, and $(v + \epsilon_v, z_1, z_2, z_3, \ldots, z_N)$, where $\epsilon_i = z_i \times 10^{-3}$ and $\epsilon_v = v \times 10^{-3}$. Numerical partial derivatives of c, d, and e are found from the three points.

(3) New values of v, z_1, z_2 (and z_3) are found in a three-dimensional Newton-Raphson iteration.

(4) Steps 1 through 3 are repeated until convergence is obtained; that is, until $c = d = e = 0$.

(5) Coefficient f is evaluated at the tricritical point. If f is greater than zero, a locally stable tricritical point has been found.

Local stability of a tricritical point is only a preliminary indication of stability. Global stability must be checked by other means.

Solution Procedure Evaluation

The models used are the Soave-Redlich-Kwong (Soave, 1972) and the Peng-Robinson (1976) equations of state. The coefficients of the $m(\omega_i)$ function in the Soave-Redlich-Kwong equation are those given by Graboski and Daubert (1978).

FORTRAN programs have been written for each of the solution procedures. The programs were first run on a Honeywell DPS 8/70 computer with a 72 bit word size (double precision). On this machine, however, the results of the numerical differentiations were subject to round-off and truncation error. In order to eliminate differentiation step size as a factor in the results of the tricritical point calculations, all computations reported here were performed on a CDC CYBER 860 computer, which has a word size of 128 bits (double precision). The algorithms described here can be run on machines

Table 1. Composition Initialization for 2-D Routine

System	Initial z_1 and z_2	Converged z_1	Converged z_2
$C_2H_6 + nC_5H_{12} + CH_4$	0.010, 0.032	0.0416	0.0174
$C_3H_8 + nC_5H_{12} + CH_4$	0.009, 0.024	0.0205	0.0145
$nC_4H_{10} + nC_5H_{12} + CH_4$	0.007, 0.020	0.0186	0.00829
$C_2H_6 + nC_6H_{14} + CH_4$	0.005, 0.032	0.1020	0.0110
$C_3H_8 + nC_5H_{12} + CH_4$	0.005, 0.024	0.0430	0.00747
$nC_4H_{10} + nC_6H_{14} + CH_4$	0.004, 0.018	0.0270	0.00281

with a 72 bit word size in double precision, but with slackened conversion criteria on the d and e coefficients of $|d| \le 10^{-4}$ and $|e| \le 10^{-4}$. The mole fractions in that case will be converged to about four significant figures.

One basis for comparison of the two solution procedures is to determine under what conditions each one fails. Failure could occur by: the temperature becoming negative; the volume becoming less than the mixture co-volume, b_m in the equation of state; or one of the mole fractions becoming negative. As mentioned earlier, both routines use the same robust method for solving $\beta = 0$ for the temperature. With this method, negative temperature was never encountered. However, either of the other constraints might be violated, depending on the initiation strategy.

In the 2-D search routine, only two variables, z_1 and z_2, need to be initialized. The fact that these compositions must satisfy the conditions: $z_1 > 0$ and $z_2 > 0$, and $z_1 + z_2 < 1$ defines the range of values in which the initial guesses must be selected. For the 3-D routine, the volume (v) must also be initialized. The critical volume of a mixture must lie in the range $b_m < v < 4b_m$ for either the Soave-Redlich-Kwong or Peng-Robinson equation.

As one means of comparing the procedures, the initiation was performed with each independent variable increased by a certain percentage above the known tricritical values. This test was performed on the systems methane + ethane + n-octane, methane + ethane + n-pentane, and methane + propane + n-pentane. Using the 2-D procedure, each of the two composition variables could be initialized at a value up to 50% higher than the converged value without failure of the routine. Using the 3-D procedure, the two composition variables and the volume could only be initialized at a maximum of 20% higher than their converged values without failure of the routine. This test gives an indication of how much more accurate the initial guesses must be for the 3-D routine to locate tricritical points.

One option available for initializing the 2-D procedure is to set z_1 and z_2 to the same initial value. This method was found to be very successful for ternary systems of light alkanes and reduced the task of initiating the procedure to the selection of one composition value. Some examples of initial values and converged values of composition are shown in Table 1. The range of values shown in column two indicates the values that both z_1 and z_2 can be initialized at and still achieve convergence. The results shown in the table were all obtained using the Soave-Redlich-Kwong equation of state with all binary interaction parameters set to zero.

Table 2. Computation Times for the System $C_3H_8 + nC_5H_{12} + CH_4$

Outer Loop Iterations	2-D Routine Time (CPU s)	3-D Routine Time (CPU s)
4	8.58	2.16
5	10.59	2.55
6	12.90	2.92
7	14.92	3.30

Setting $z_1 = z_2$ may also be used with the 3-D routine, reducing the number of values which must be selected to one composition and one volume. It was found particularly advantageous to set the volume to a value in the middle of its range $v = 2.5b_m$, and to initialize $z_1 = z_2$ at a number of compositions until convergence is achieved.

Once an initiation point which allows direct convergence to the tricritical point is located, the 3-D routine runs 3 to 4 times faster than the 2-D routine. The computation times on the CDC CYBER 860 for a number of calculations performed on the system methane + propane + n-pentane are shown in Table 2. The two routines are compared on the basis of computation time for a given number of outer loop iterations. Of course, the 3-D search routine must be initiated at a point much closer to the tricritical conditions in order to converge in the same number of outer loop iterations as the 2-D search routine. All times given in Table 2 reflect approximately 0.5 s of CPU time required for loading the data file, selecting the components, selecting the equation of state and setting other program options.

From Table 2 it can be seen that, even when three more iterations are required, the 3-D procedure is still 2.5 times faster then the 2-D procedure.

Systems with a critical point at the tricritical composition

The 2-D procedure fails to locate the tricritical point in the mixture methane + n-hexane + hydrogen sulfide. The c function is plotted against (v/b_m) for the tricritical mixture in this system in Figure 1. As is clear from the figure, $c = 0$ is satisfied by more than one volume. For this mixture, the largest volume root corresponds to an ordinary critical point and the next is the tricritical volume. The 2-D procedure is initialized at $(v/b_m) = 4$, and is therefore designed to converge only to the largest root. The existence of multiple solutions to the ordinary critical point problem is ultimately the source of the failure of the 2-D routine to locate the tricritical point in mixtures of this kind.

Locating all the ordinary critical points of a mixture, as was discussed by Heidemann and Khalil (1980), might require computing the c coefficient over the whole applicable range of (v/b_m) and searching for sign changes around which to initiate the computation.

The 2-D search routine can be used for systems with tricritical points located at the largest root in volume when more than one critical point exists. The 3-D routine must be used for all others.

Location of multiple tricritical points

Recent work by Diandreth and Paulaitis (1989) has indicated that some ternary systems have more than one tricritical point. The calculation of multiple tricritical points with the solution procedures presented here is essentially a problem of initiation strategies.

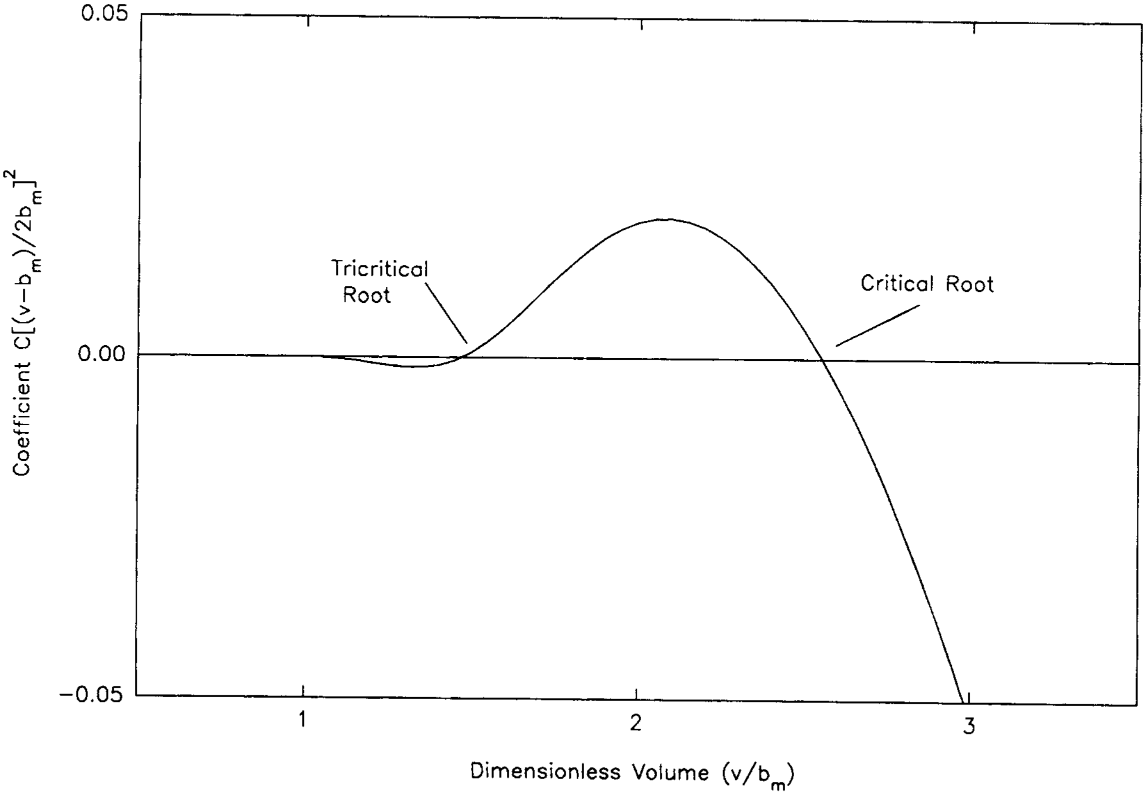

Figure 1. Coefficient *c* as a function of volume for the system methane + *n*-hexane + hydrogen sulfide at the tricritical composition.

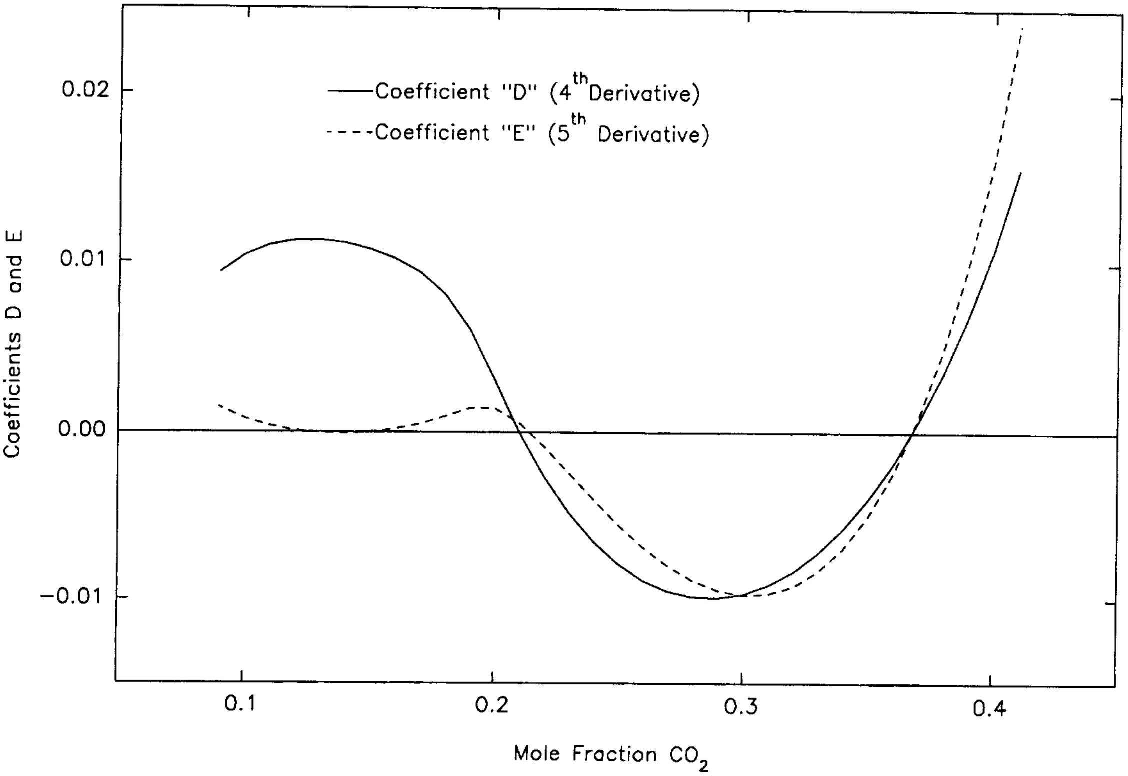

Figure 2. Coefficients *d* and *e* for the system water + isopropanol + carbon dioxide, mole fraction $H_2O = 0.5284$.

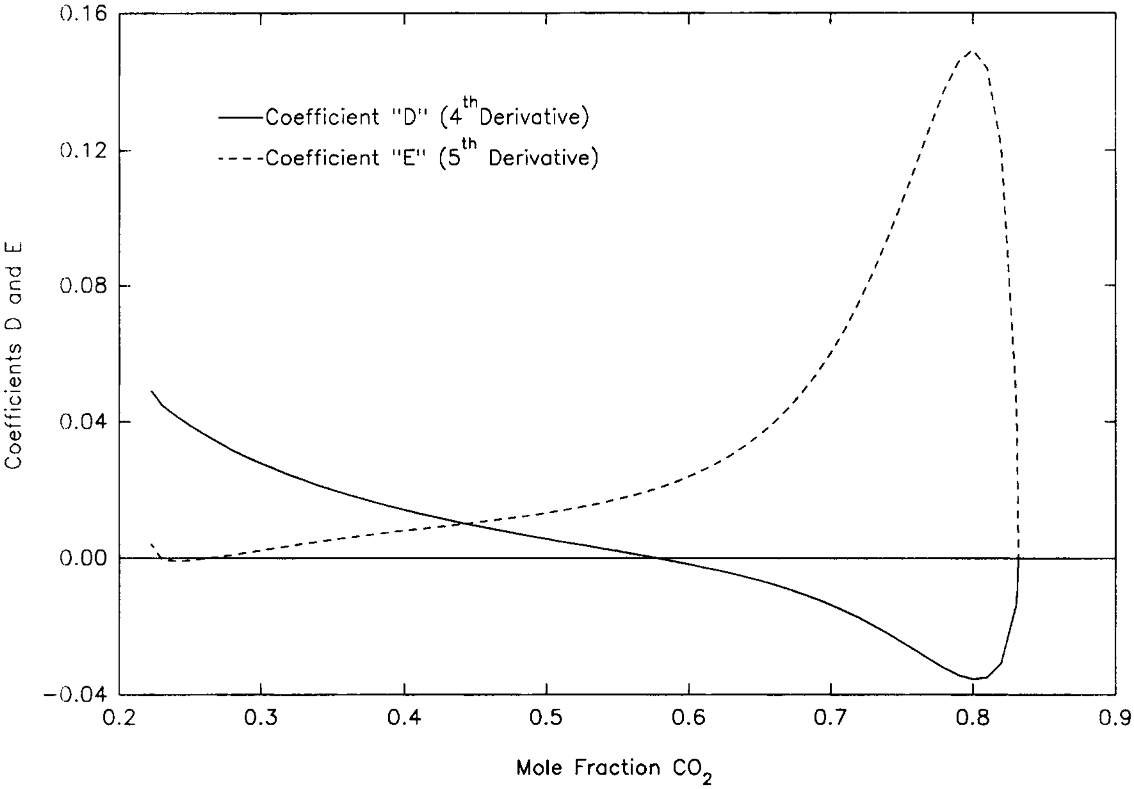

Figure 3. Coefficients *d* and *e* for the system water + isopropanol + carbon dioxide, mole fraction $H_2O = 0.07217$.

Figures 2 and 3 show the values of the *d* and *e* functions plotted vs. the value of one mole fraction in the vicinity of each of the two tricritical points found for the system water + isopropanol + carbon dioxide. The plots are generated by calculating the critical temperature and volume for a given composition $b = c = 0$, then evaluating coefficients *d* and *e*. The tricritical point is then seen as the point where *d* and *e* are both zero simultaneously. In Figure 3, the functions appear to terminate on the axis, but they actually intersect and terminate at a slightly higher mole fraction of carbon dioxide. If the carbon dioxide mole fraction exceeds the terminating value there are no critical points of any kind. For both of the tricritical compositions shown in these figures, the tricritical volume corresponds to an intermediate root of the *c* function and the 3-D search routine must be used to locate the tricritical coordinates.

Figures 2 and 3 also give an indication of the difficulty of locating some tricritical points. In Figure 2, it can be seen that selecting a mole fraction of carbon dioxide anywhere from 0.3 to 0.4 will send the search routine in the direction of the tricritical point. For the conditions of Figure 3, on the other hand, the mole fraction of carbon dioxide must be selected in the range 0.82 to 0.83 for convergence to the solution shown. Any other guess will result in failure or convergence to the other tricritical point.

Summary of solution procedure evaluation

From the above discussion, it can be seen that it is impossible to locate the full range of critical and tricritical behavior for any given system using just one of the two solution procedures. The 2-D routine is easier to initiate for many systems but fails completely for others. Initiating the 3-D procedure is more difficult, but the routine is faster and will find a tricritical point in some systems where the 2-D procedure will not. Locating more than one tricritical point in a system is possible only with care.

Michelsen and Heidemann (1988) used a four-dimensional search routine to handle systems for which the 2-D routine was found to fail. They noted that this procedure must be initiated at a point very close to the tricritical or the routine will fail, and all four variables must be initialized by the user. The 3-D routine proposed here has all the capabilities of the 4-D procedure and is much more "forgiving," since the only unbounded variable, temperature, does not require initialization.

Tricritical Points in Ternary Systems

Ternary systems have been studied because of the availability of experimental data and also because even these systems exhibit a wide range of complex behavior.

Database

To calculate tricritical points using equations of state, the usual pure component database consisting of critical temperature, critical pressure, and acentric factor is required. In addition, binary interaction parameters may also be included. Critical temperatures, critical pressures and acentric factors have been taken from Reid, Prausnitz and Poling (1987). Some of the acentric factors are the values recalculated from vapor

Table 3. Comparison of Calculated and Experimental Tricritical Coordinates

	T (K)	P (MPa)	v (m^3/kmol)	x_2 (mol %)	x_3 (mol %)
$CH_4 + C_2H_6 + nC_8H_{18}$					
Experimental (*)	222.0	6.991	0.0610	20.0	3.50
Soave-Redlich-Kwong, $k_{ij}=0$	225.8	7.001	0.0807	22.2	0.65
Soave-Redlich-Kwong, $k_{ij}\neq0$	236.3	7.629	0.0798	29.2	1.27
Peng-Robinson, $k_{ij}=0$	221.7	6.785	0.0722	19.6	0.64
Peng-Robinson, $k_{ij}\neq0$	234.0	7.556	0.0708	28.1	1.40
$CH_4 + C_3H_6 + nC_8H_{18}$					
Experimental (*)	215.3	7.113	0.0620	10.6	1.55
Soave-Redlich-Kwong, $k_{ij}=0$	210.0	6.564	0.0747	7.84	0.35
Soave-Redlich-Kwong, $k_{ij}\neq0$	215.7	7.183	0.0724	11.5	0.55
Peng-Robinson, $k_{ij}=0$	208.3	6.400	0.0676	7.05	0.37
Peng-Robinson, $k_{ij}\neq0$	215.1	7.122	0.0650	11.5	0.61
$CH_4 + nC_4H_{10} + nC_8H_{18}$					
Experimental (*)	207.3	6.520	0.0605	6.20	0.96
Soave-Redlich-Kwong, $k_{ij}=0$	201.1	5.808	0.0749	3.45	0.077
Soave-Redlich-Kwong, $k_{ij}\neq0$	202.7	5.989	0.0736	4.53	0.038
Peng-Robinson, $k_{ij}=0$	200.8	5.786	0.0677	3.31	0.11
Peng-Robinson, $k_{ij}\neq0$	203.2	6.047	0.0657	4.86	0.069
$CH_4 + CO_2 + nC_8H_{18}$					
Experimental (*)	222.0	7.306	0.0578	29.9	3.65
Soave-Redlich-Kwong, $k_{ij}=0$	221.5	6.926	0.0735	22.6	0.38
Soave-Redlich-Kwong, $k_{ij}\neq0$	215.9	6.528	0.0735	23.3	0.43
Peng-Robinson, $k_{ij}=0$	218.0	6.701	0.0666	19.6	0.40
Peng-Robinson, $k_{ij}\neq0$	215.1	6.488	0.0659	22.7	0.49
$CH_4 + N_2 + nC_4H_{10}$					
Experimental (**)	175.5	6.219	0.0547	23.5	12.3
Soave-Redlich-Kwong, $k_{ij}=0$	187.1	6.053	0.0711	17.5	2.62
Soave-Redlich-Kwong, $k_{ij}\neq0$	196.9	6.123	0.0722	6.34	3.97
Peng-Robinson, $k_{ij}=0$	181.8	6.059	0.0626	24.0	2.38
Peng-Robinson, $k_{ij}\neq0$	194.0	6.239	0.0637	9.65	4.01
$CO_2 + C_2H_6 + CH_3OH$					
Experimental (†)	306.7	7.772	0.0608	18.0	10.0
Soave-Redlich-Kwong, $k_{ij}\neq0$	322.8	9.428	0.0734	15.3	12.0
Peng-Robinson, $k_{ij}\neq0$	319.6	9.150	0.0666	17.7	11.5
$CO_2 + CH_3OH + H_2O$					
Experimental (‡)	317.8	8.917	—	13.2	0.81
Soave-Redlich-Kwong, $k_{ij}\neq0$	339.1	11.614	0.0639	14.4	2.80
Peng-Robinson, $k_{ij}\neq0$	338.2	11.560	0.0571	14.3	2.88
$CO_2 + C_2H_5OH + H_2O$					
Experimental (‡‡)	320.6	9.292	—	15.0	2.00
Soave-Redlich-Kwong, $k_{ij}\neq0$	334.1	11.180	0.0643	9.19	4.95
Peng-Robinson, $k_{ij}\neq0$	334.1	11.283	0.0560	9.08	6.04

(*) Kohn and Luks (1981); (**) Kohn et al. (1983); (†) Efremova and Shvarts (1972); (‡) Efremova and Shvarts (1966, 1969); (‡‡) Shvarts and Efremova (1970).

pressure correlations by Trebble (1989). The main source of binary interaction parameters is Oellrich et al. (1981), while some parameters are obtained from Reid, Prausnitz and Poling (1987). Parameters for the alcohol and carbon dioxide water systems were based on the work of Diandreth and Paulaitis (1989). All the parameters used are tabulated in Kohse (1989).

Comparison to experimental data

Kohse (1989) tabulated data for 15 ternary systems with experimentally located tricritical points. An attempt was made to calculate tricritical points for all 15 systems. For eight of these systems, tricritical points were located using the methods outlined here; tricritical points could not be located for the other seven. Of these seven, four contain pentane in combination with methane, and failure is due to the incorrect prediction of liquid-liquid immiscibility for the methane + pentane binary pair by the equation of state thermodynamic model. One system consists of n-butane + acetic acid + water, and failure most likely results because of the inadequacy of the equation of state in describing acetic acid. The final two failures are for systems with ethane and heavy alkanes; these failures are also a consequence of nonphysical predictions by the equations of state of liquid-liquid separations, between ethane and the heavy alkane in this case. The equations of state predict liquid phase separations in the ethane-hexadecane pair and in all higher alkanes, but the data show separations first with octadecane (Specovius et al., 1981).

The experimental and calculated tricritical coordinates for the eight systems are shown in Table 3. For each system the calculations were performed with both the Soave-Redlich-

Table 4. Systems with Simultaneously Occurring Critical and Tricritical Points

	$CH_4/nC_6H_{14}/H_2S$	$CH_4/CO_2/H_2S$	$CO_2/C_2H_6/CH_3OH$
mol % x_1	53.57	63.56	72.67
mol % x_2	2.50	22.58	15.35
mol % x_3	43.93	13.86	11.98
Tricritical			
P (MPa)	10.77	8.19	9.43
T (K)	224.4	232.6	322.79
v (m^3/kmol)	0.04940	0.06254	0.07344
Critical			
P (MPa)	14.30	8.18	2.94
T (K)	299.4	232.5	291.37
v(m^3/kmol)	0.08091	0.06248	0.06107

Kwong and Peng-Robinson equations of state, and, where possible, with and without binary interaction parameters.

The first five systems shown in this table are mixtures of alkanes up to n-octane and the light gases CO_2 and N_2. For each of these systems, the calculated tricritical temperature and pressure compare favorably with the experimental values. Relative errors in the calculated tricritical volumes are larger. The calculated tricritical compositions show the largest error in comparison with the experimental values. The calculated mole fraction of the heavy alkane is always underestimated in comparison to the experimental value; in some cases it is ten times less than the experimental value. The use of binary interaction parameters improves the calculation of heavy alkane concentration, however, the errors remain large. In the case of the methane + nitrogen + n-butane system, use of the interaction parameters gives a small decrease in the error of the heavy alkane concentration, at the cost of a large increase in the error of the nitrogen concentration. Errors in the calculated tricritical temperatures and pressures decrease in some cases if binary interaction parameters are used and increase in others.

The last three systems shown in the table contain the polar components water, methanol and ethanol. For these systems, tricritical points could not be located with the binary interaction parameters set to zero. The calculated tricritical temperature, pressure and volume show larger errors in these systems than in the first five; however, composition values show slightly smaller errors. The sometimes large errors between calculated and experimental tricritical conditions, as well as the high sensitivity of the calculations to input data, demonstrate the importance of the binary interaction parameters in these calculations.

Table 5. Tricritical Points in the Ternary System $CO_2 + IPA + H_2O$

	Diandreth and Paulaitis (1989)		This Work	
	TCP 1	TCP 2	TCP 1	TCP 2
P (MPa)	26.27	10.89	28.95	11.84
T (K)	407.15	335.15	426.36	340.08
v (m^3/kmol)	—	—	0.04008	0.05735
mol % CO_2	—	—	36.77	83.18
mol % IPA	—	—	10.38	9.61
mol % H_2O	—	—	52.85	7.21

Multiple critical and tricritical points

Table 4 indicates calculated tricritical points for three ternary systems and separate (ordinary) critical points for the three tricritical mixtures. All of the values given in this table are calculated using the Soave-Redlich-Kwong equation of state with nonzero binary interaction parameters and none of the systems have been studied experimentally so the calculations are "predictive." These calculations are presented in order to show the nature of the computational problem.

Calculated pressure-temperature diagrams for the three tricritical systems of Table 4 show the tricritical point at the top of a three-phase region. For the first system shown, the tricritical point has a much smaller molar volume than the critical point and the 3-D search procedure must be used to locate the tricritical point. The second system shown in the table has a phase diagram similar to the first, however, the tricritical point exists at a larger volume than the critical point. As can be seen in the table, these two points are almost indistinguishable. The difference in molar volume between the two is 6×10^{-5} m^3/kmol. This indicates that the two roots of the c function in volume are very close together, and a slight change in composition will cause the c curve to shift below the axis, giving the case where there are no critical points of any kind. The position of the c coefficient function also requires that the 3-D routine be used to solve for the tricritical point, despite the fact that the tricritical volume is larger than the critical volume. The perturbation of composition in the outer loop of the 2-D routine will cause the c curve to shift below the axis leading to failure of the routine. In the 3-D routine, the simultaneous variation of composition and volume allows convergence to the tricritical point.

The third system given in the table is an example of one in which the tricritical point has a much larger molar volume than the critical point, allowing the location of the tricritical point with the 2-D solution procedure. Again, this system is expected to have a three-phase region connected to the tricritical point.

Diandreth and Paulaitis (1989) report the location of two tricritical points for the ternary mixture isopropanol + water + carbon dioxide. Since the tricritical point of a ternary system is an isolated point, a ternary system with two tricritical points must have two different types of three-phase equilibria. This implies that the system is capable of four-phase equilibria. Diandreth and Paulaitis (1989) have made experimental measurements of L_1-L_2-V, $L_1-L_2-L_3$ and $L_1-L_2-L_3-V$ equilibria for the mixture, and used these data for the regression of binary interaction parameters for the Peng-Robinson equation of state. They present a phase diagram calculated via successive multiphase flash calculations showing three-phase and four-phase regions and the two tricritical points. One tricritical point is at the termination point of a L_1-L_2-V three-phase region, while the other is at the termination point of a L_2-L_3-V three-phase region.

Two tricritical points have been calculated using the direct calculation procedures presented here and the Peng-Robinson equation of state with pure component and mixture parameters that were given by Diandreth and Paulaitis (1989). Both tricritical points were located using the 3-D search routine, as each one is a tricritical point with an ordinary critical point occurring simultaneously at a larger molar volume.

The tricritical coordinates calculated by us and those pre-

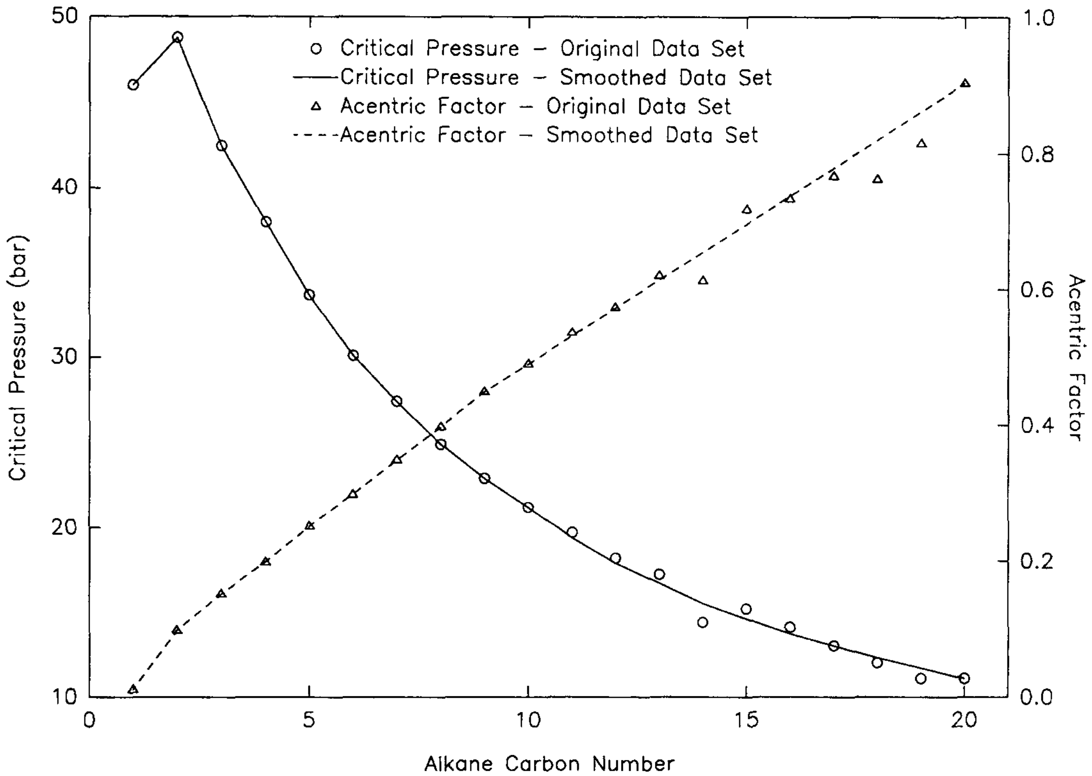

Figure 4. Pure component critical pressure and acentric factor data for alkanes as a function of carbon number.

sented by Diandreth and Paulaitis (1989) are shown in Table 5. There are some significant differences. Since the same thermodynamic model was used in both sets of calculations, the differences in the tricritical coordinates must lie in the calculation methods. Precise determination of the tricritical coordinates would be very difficult with multiphase flash calculations because the 3-phase regions are very narrow and because flash calculations show poor convergence behavior around critical points in general. We believe that the differences between our direct calculations and the Diandreth and Paulaitis (1989) extrapolations in Table 5 show the benefit of having available a direct computational method.

Homologous series of alkanes and light gases

Tricritical points have been calculated for five homologous series. The components were chosen so that one system in each series could be compared to experimentally located tricritical conditions. The five series are as follows:

(1) $CH_4 + C_2H_6 + nC_NH_{2N+2}$
(2) $CH_4 + C_3H_8 + nC_NH_{2N+2}$
(3) $CH_4 + nC_4H_{10} + nC_NH_{2N+2}$
(4) $CH_4 + CO_2 + nC_NH_{2N+2}$
(5) $CH_4 + N_2 + nC_NH_{2N+2}$

For each series, the third and heaviest component in the system is a normal alkane with carbon number (N).

The critical pressure and acentric factor data for the normal alkanes from *n*-decane to *n*-eicosane do not follow the smooth trends exhibited by the lower carbon number alkanes, as can be seen in Figure 4. Smoothed values were obtained simply by interpolating between the values at *n*-decane and *n*-eicosane using linear interpolation for the acentric factor, and hyperbolic interpolation for the critical pressure. The smoothed data are also shown in Figure 4. The pure component critical temperature data do not show significant fluctuations and were not smoothed.

The five homologous series exhibit similar trends when the tricritical temperature, pressure, molar volume and mole fractions are plotted as a function of the carbon number of the third component. The tricritical temperature and the tricritical mole fraction of the heavy component for series 2 are shown as functions of the carbon number of the heavy component in Figures 5 and 6, respectively. The results were calculated using the Soave-Redlich-Kwong equation with all binary interaction parameters k_{ij} equal to zero, the Soave-Redlich-Kwong equation with $k_{ij} \neq 0$ and the Soave-Redlich-Kwong equation with the smoothed data set and $k_{ij} \neq 0$.

The range of carbon number of the third component for which tricritical behavior will be exhibited by a system varies for each of the above five systems. For series 1, the lower limit on the carbon number range is 5, while the upper limit depends on which equation of state is used. With the Soave-Redlich-Kwong equation, the upper limit is 14; with the Peng-Robinson equation the upper limit is 19. Series 2, 3 and 4 all have lower carbon number limits of 5, and upper limits above 20. Series 5 has the smallest range, with carbon numbers of 2, 3, and 4 being the only ones which enable tricritical points to be calculated.

For series 5, experimental work indicates that the upper limit on the carbon number of the third component is 5. Kohn et al. (1983) present tricritical point coordinates for the methane + nitrogen + *n*-pentane system and demonstrate that methane + nitrogen + *n*-hexane will not have a tricritical point due to

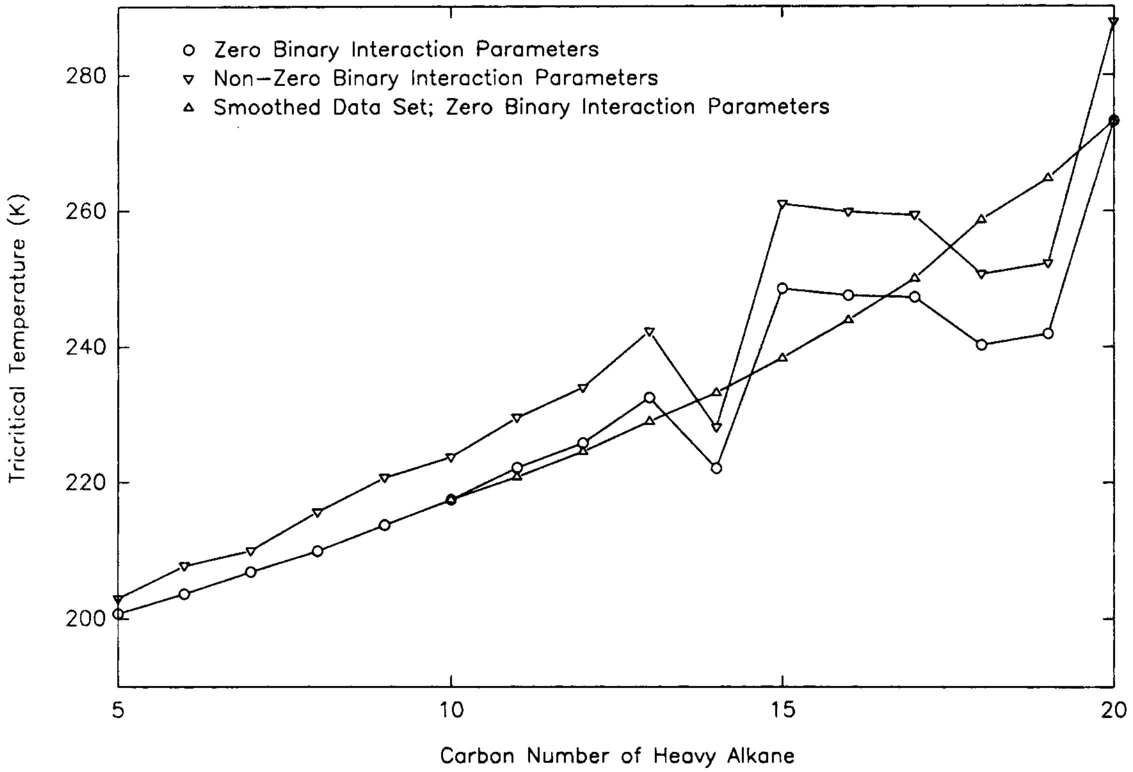

Figure 5. Tricritical temperature for the ternary alkane systems methane + propane + $n-C_NH_{2N+2}$.

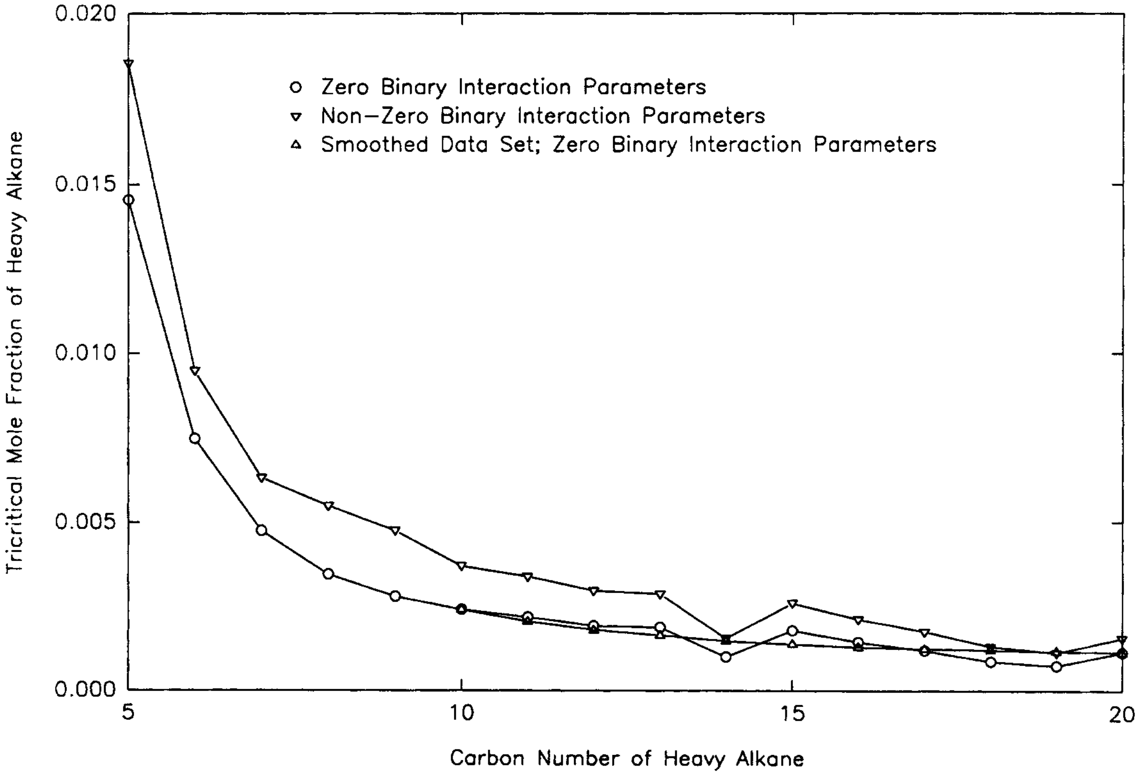

Figure 6. Mole fraction of heavy component at the tricritical point for the ternary alkane systems methane + propane + n-C_NH_{2N+2}.

the appearance of the methane + n-hexane three-phase coexistence line. The inability of the model to locate a tricritical point for the methane + nitrogen + n-pentane system is due to the equations of state incorrectly predicting liquid-liquid immiscibility for the methane + n-pentane binary pair. This immiscibility only occurs with alkanes of carbon number of 6 or higher. This is also the reason that the models are unable to locate tricritical points for any systems in the series $CH_4 + nC_5H_{12} + nC_NH_{2N+2}$. Kohn et al. (1982) present tricritical coordinates for one system in this series: ethane + n-pentane + n-octane, however, no tricritical point for this system could be located with the present model.

The trends shown in Figures 4 and 5 are, in general, exhibited by each of the homologous series. The tricritical temperature increases with the carbon number of the heavy component in all the series. The tricritical pressure apparently tends towards an upper limit and actually has a maximum in series 1. Tricritical volume also shows a gradual increase with carbon number for all series studied. The mole fraction of the heavy component decreases rapidly in all series, while the composition of the second component shows an increase for all series except for series 6.

Model sensitivity

For all the calculated tricritical conditions, the sensitivity to binary interaction parameters k_{ij} is similar for both the Soave-Redlich-Kwong and Peng-Robinson equations. Some specific results were shown in Table 3. The calculated tricritical volume appears to show little sensitivity to the k_{ij} values. Temperature and pressure are sensitive to the k_{ij} values, however, it is the concentrations of the components which show the largest variation. The concentration of the third component, the heavy alkane, showed the most variation. Use of binary interaction parameters can double the tricritical concentration of these components.

From Figure 4 it can be seen that the variations in the pure component data introduced by smoothing the data are small. The sensitivity of the calculated tricritical points to the small changes introduced by smoothing the pure component data is very large, as can be seen in Figures 5 and 6.

Characteristics of Ternary Tricritical Systems

Two types of tricritical points

Michelsen (1986) has demonstrated that there are two types of tricritical points found in fluid mixtures. He demonstrated that the approach to the tricritical point in ternary systems may be seen in composition space as three-phase triangles decreasing in size down to a point as the tricritical temperature and pressure is reached. One type of tricritical point has a composition which lies on the limit of, but outside, the three-phase composition triangles. The second type has a tricritical composition which is inside the three-phase region. In P-T space, no three-phase region exists at the tricritical composition for the first type, while the tricritical point and a three-phase region exist simultaneously for the second type. Michelsen (1986) has presented examples of such phase boundaries.

All of the tricritical points in the homologous series presented here have tricritical points of the first type. Several of the other systems reported here have tricritical points of the second type. These include water + isopropanol + carbon dioxide and water + ethanol + carbon dioxide.

Phase boundaries in the tricritical region

Phase boundaries for the tricritical mixture and two near-tricritical mixtures in the system methane + ethane + n-octane are presented in Figure 7. The near-tricritical compositions are given by specified values of parameter s which defines a distance in composition space from the tricritical composition (that is, where $s = 0.0$). The mole numbers in the mixture are given by

$$n_i = s u_i z_i^{1/2} + z_i \qquad (11)$$

where the z_i are the tricritical mole fractions and

$$u_1 = (1/3)^{1/2}, \quad u_2 = -(1/3)^{1/2} \quad \text{and} \quad u_3 = (1/3)^{1/2} \qquad (12)$$

The mole numbers are normalized to give the composition in mole fractions:

$$x_i = n_i / \Sigma n_j \qquad (13)$$

The resulting mole fractions are shown in Table 6.

The stable portions of the phase boundaries calculated for methane + ethane + n-octane with $s = 0.2$, $s = 0.1$ and $s = 0.0$ (tricritical) are shown in Figure 7. The phase boundaries were calculated at the compositions shown in Table 6 using the Soave-Redlich-Kwong equation of state with the smoothed data set and with all binary interaction parameters set to zero.

As can be seen in Figure 7, the three phase regions shrink to a point as s approaches zero (the tricritical composition).

Limits of tricritical behavior in a series

As noted earlier, tricritical points can be calculated for systems in the homologous series methane + ethane + nC_NH_{2N+2} for only a certain range of values of carbon number, N. The upper limit of N depends on the equation of state being used for the calculation, the pure component input data and the values of the binary interaction coefficients. In this section, the results obtained with the Soave-Redlich-Kwong equation of state using the smoothed data set and with the binary interaction parameters set to zero will be discussed.

With the calculation model set as described above, the lower limit of carbon number is 5. For this system the calculated tricritical composition is 94.10% methane, 4.16% ethane and 1.74% n-pentane. Increasing to a carbon number of 8, the tricritical mixture is still composed mostly of methane as follows: 77.12% methane, 22.23% ethane and 0.65% n-octane; this is comparable to the experimental tricritical composition reported for this system (Kohn and Luks, 1981). Following the series to higher carbon numbers for the third component, the model predicts that the mole fraction of methane continues to decrease, while the concentration of ethane increases. This continues until the upper limit on the carbon number is reached at $N = 15$; at this point the tricritical composition is 13.73% methane, 85.93% ethane, and 0.34% n-pentadecane. The values of tricritical concentration for methane and ethane in this series are plotted against carbon number of the heavy component in Figure 8. The series apparently terminates when the methane is "squeezed out" of the mixture.

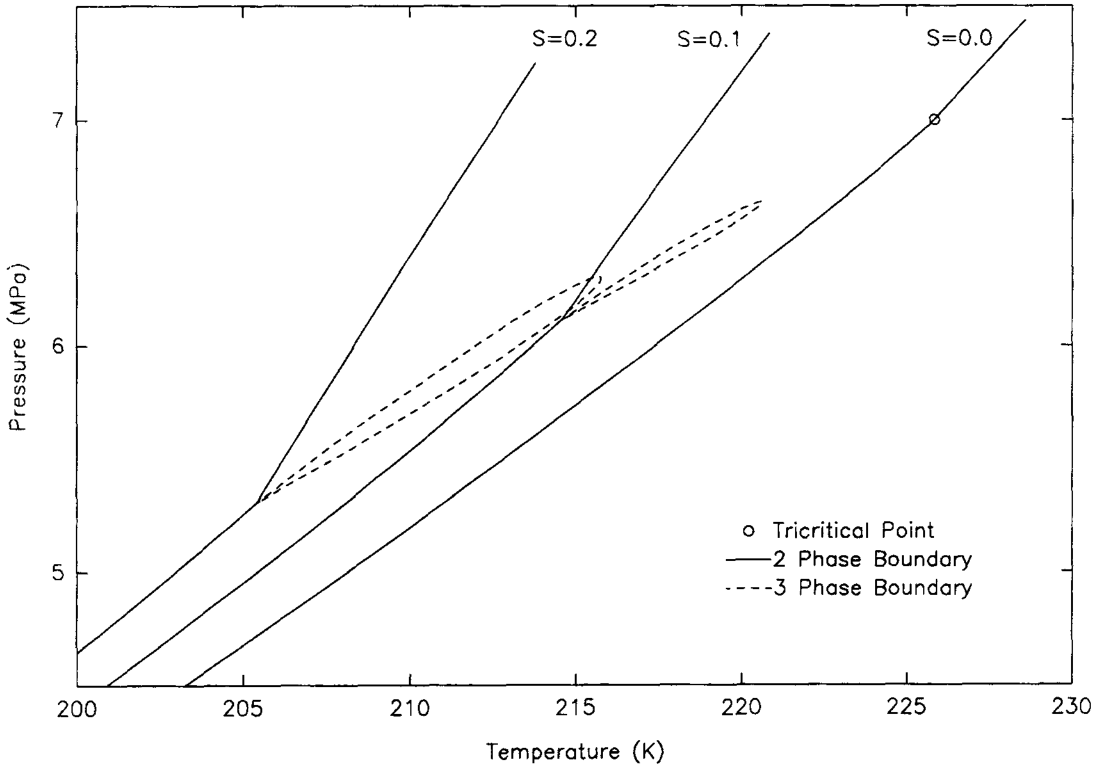

Figure 7. Phase boundaries for the system methane + ethane + *n*-octane approaching the tricritical point.

There are data for only one mixture in the homologous series with methane, ethane and a heavy alkane. It would be interesting to determine whether the predictions for the trend in the series that are shown in Figure 8 are qualitatively correct. It is already known that the equations of state predict liquid-liquid separations in the ethane-hexadecane system that do not occur experimentally, and that feature probably causes a termination of the series prematurely at $N=15$. We anticipate, however, that the principal qualitative features shown here would be verified by experiment.

Conclusions

The 2-D search procedure provides a method of locating tricritical points which is easy to initialize as only two compositions must be selected by the user and will converge with poor initial guesses. This method will fail to locate tricritical points in systems which have ordinary critical points with larger molar volumes occurring at the same composition as the tricritical points. The 3-D search procedure is somewhat more difficult to initialize as three values, volume and the two compositions, must be supplied by the user. These values must also be closer to the tricritical point for convergence to be achieved. This search routine is capable of locating tricritical points in any system regardless of other critical behavior occurring simultaneously. The 3-D routine proves to be more easily applicable than a full four-dimensional search as the need to supply an initial value for temperature is eliminated and convergence may be achieved with poorer initial guesses in the 3-D routine than in a 4-D routine.

Table 6. Near-Tricritical Compositions for the System Methane + Ethane + *n*-Octane

	$s=0.0$ (Tricritical)	$s=0.1$	$s=0.2$
mol % CH_4	77.12	82.61	79.94
mol % C_2H_6	22.23	15.89	18.98
mol % nC_8H_{18}	0.65	1.49	1.08

It appears unlikely that tricritical point calculations could become a routine element in process simulation programs. A considerable amount of user intervention may be required to obtain convergence, whichever of the computational approaches we examined was chosen for implementation. Furthermore, a tricritical point is a fixed point only in a ternary system. Some features of quaternary systems with tricritical points have been described in a recent article by us (Kohse and Heidemann, 1992).

Comparison of experimentally located tricritical points in systems of alkanes and light gases to those calculated with the Peng-Robinson and Soave-Redlich-Kwong equations of state shows that both models provide results which are substantially in error. The tricritical mole fraction values show the largest errors; the use of nonzero binary interaction parameters reduces the error in these concentration values. The solution procedures developed here are capable of locating critical and tricritical points in systems with complex multiphase behavior. The search for tricritical points has indicated that there is a wide range of multiphase behavior occurring even in simple ternary systems.

Acknowledgment

This research was supported by a grant from the National Sciences

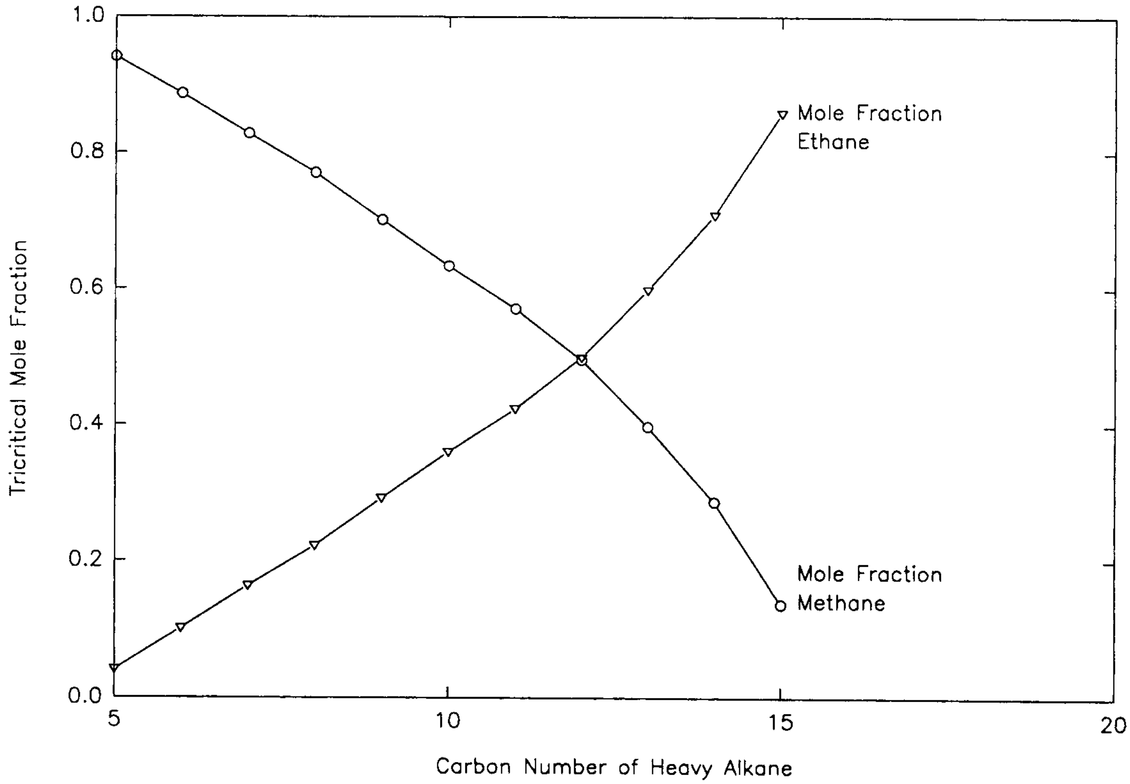

Figure 8. Tricritical concentration of components in the systems $C_1 + C_2 + n - C_NH_{2N+2}$.

and Engineering Research Council of Canada and a grant from Imperial Oil of Canada.

Notation

a_m, b_m = equation of state parameters for the mixture
A = Helmholtz free energy
$\boldsymbol{B}$ = Hessian of F
B_{ij} = element of $\boldsymbol{B}$
b, c, d, e, f = coefficients in the Taylor series expansion of the tangent plane distance
f_i = fugacity of component i
F = tangent plane distance
F_s = derivative of F with respect to s
$\boldsymbol{g}$ = gradient of F in X
g_i = element of $\boldsymbol{g}$
h = step size for numerical differentiation
k_{ij} = binary interaction parameter
$\boldsymbol{n}$ = vector of mole numbers
n_i = element of $\boldsymbol{n}$
N = number of components
$\boldsymbol{p}$ = vector of third derivatives of $\boldsymbol{g}$ with respect to s
p_i = element of $\boldsymbol{p}$
P = pressure
$\boldsymbol{q}$ = vector in the Taylor series expansion of X
q_i = element of $\boldsymbol{q}$
$\boldsymbol{r}$ = vector of second derivatives of $\boldsymbol{g}$ with respect to s
r_i = element of $\boldsymbol{r}$
R = universal gas constant
s = distance parameter in composition space
T = temperature
$\boldsymbol{u}$ = eigenvector of matrix $\boldsymbol{B}$
u_i = element of $\boldsymbol{u}$
v = molar volume
V = volume
$\boldsymbol{w}$ = vector in the Taylor series expansion of X
w_i = element of $\boldsymbol{w}$
X = vector of scaled and translated mole numbers
X_i = element of X
z = vector of mole fractions
z_i = element of z

Greek letters

ϵ = perturbation step size
μ = chemical potential
ω = acentric factor

Subscripts

i, j, k = component indices
0 = initial state

Literature Cited

Abramowitz, M., and I. A. Stegun, *Handbook of Mathematical Functions*, Dover, New York (1965).

Baker, L. E., and K. D. Luks, "Critical Point and Saturation Pressure Calculations for Multicomponent Systems," *Soc. Petroleum Engrs. J.*, **20**, 15 (1980).

Cheney, E. W., and D. R. Kincaid, *Numerical Mathematics and Computing*, 2nd ed., Brooks/Cole, Monterey, CA (1985).

Diandreth, J. R., and M. E. Paulaitis, "Multiphase Behavior in Ternary Fluid Mixtures: A Case Study of the Isopropanol-Water-CO_2 System at Elevated Pressures," *Chem. Eng. Sci.*, **44**, 1061 (1989).

Efremova, G. D., and A. V. Shvarts, "The Critical Point for Liquid-Liquid-Gas Three-Phase Equilibrium in the System Methanol-Water-Carbon Dioxide," *Zh. Fiz. Khim.*, **40**, 907 (1966). (*Russ J. Phys. Chem.*, **40**, 486.)

Efremova, G. D., and A. V. Shvarts, "Higher-Order Critical Phenomena in Ternary Systems," *Zh. Fiz. Khim.*, **43**, 1732 (1969). (*Russ. J. Phys. Chem.*, **43**, 968.)

Efremova, G. D., and A. V. Shvarts, "Higher-Order Critical Phenomena in Ternary Systems. The Methanol-Carbon Dioxide-Ethane System," *Zh. Fiz. Khim.*, **46**, 408 (1972). (*Russ. J. Phys. Chem.*, **46**, 237.)

Fox, J. R., "Tricritical Phenomena in Ternary and Quaternary Fluid Mixtures," *J. Chem. Phys.*, **69**, 2231 (1978).

Gibbs, J. W., "On the Equilibrium of Heterogeneous Substances, Part I," *Trans. of the Connecticut Academy*, **3**, 108 (1876). As reprinted in: *The Scientific Papers of J. Willard Gibbs*, Vol. 1, Dover, New York (1961).

Graboski, M. S., and T. E. Daubert, "A Modified Soave Equation of State for Phase Equilibrium Calculations. 1: Hydrocarbon Systems," *Ind. Eng. Chem. Process Des. Dev.*, **17**, 443 (1978).

Griffiths, R. B., "Thermodynamic Model for Tricritical Points in Ternary and Quaternary Fluid Mixtures," *J. Chem. Phys.*, **60**, 195 (1974).

Heidemann, R. A., and A. M. Khalil, "The Calculation of Critical Points," *AIChE J.*, **26**, 769 (1980).

Knobler, C. M., and R. L. Scott, "Multicritical Points in Fluid Mixtures: Experimental Studies," *Phase Transitions and Critical Phenomena*, Vol. 9, C. Domb and J. L. Lebowitz, eds., Academic Press (1984).

Kohn, J. P., and K. D. Luks, "Liquid-Liquid-Vapor Equilibria in Cryogenic LNG Mixtures," *Research Report RR-49*, Gas Processors Association, Tulsa, OK (1981).

Kohn, J. P., R. C. Merrill, and K. D. Luks, "Liquid-Liquid-Vapor Equilibria in Cryogenic LNG Mixtures. Phase II," *Research Report RR-60*, Gas Processors Association, Tulsa, OK (1982).

Kohn, J. P., R. C. Merrill, and K. D. Luks, "Liquid-Liquid-Vapor Equilibria in Cryogenic LNG Mixtures. Phase III—Nitrogen Rich Systems," *Research Report RR-67*, Gas Processors Association, Tulsa, OK (1983).

Kohse, B. F., "The Calculation of Tricritical Points," M.Sc. Thesis, The University of Calgary, Calgary, Alberta, Canada (1989).

Kohse, B. F., and R. A. Heidemann, "Tricritical Lines and Multiphase Equilibria in Quaternary Mixtures," *Fluid Phase Equilib.*, **75**, 11 (1992).

Luks, K. D., "The Occurrence and Measurement of Multiphase Equilibria Behavior," *Fluid Phase Equilib.*, **29**, 209 (1986).

Michelsen, M. L., "The Isothermal Flash Problem. Part II. Phase Split Calculation," *Fluid Phase Equilib.*, **9**, 21 (1982).

Michelsen, M. L., "Calculation of Critical Points and Phase Boundaries in the Critical Region," *Fluid Phase Equilib.*, **16**, 57 (1984).

Michelsen, M. L., "Some Aspects of Multiphase Calculations," *Fluid Phase Equilib.*, **30**, 15 (1986).

Michelsen, M. L., and R. A. Heidemann, "Calculation of Tri-Critical Points," *Fluid Phase Equilib.*, **39**, 53 (1988).

Oellrich, L., U. Plöcker, J. M. Prausnitz, and H. Knapp, "Equation-of-State Methods for Computing Phase Equilibria and Enthalpies," *Int. Chem. Eng.*, **21**, 1 (1981).

Peng, D.-Y., and D. B. Robinson, "A New Two-Constant Equation of State," *Ind. Eng. Chem. Fundam.*, **15**, 59 (1976).

Pend, D.-Y., and D. B. Robinson, "A Rigorous Method for Predicting the Critical Properties of Multicomponent Systems from an Equation of State," *AIChE J.*, **23**, 137 (1977).

Reid, R. C., J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill, New York (1987).

Scott, R. L., "Multicritical Phenomena in Fluid Mixtures," *Proceedings of the Eighth Symposium on Thermophysical Properties, Vol. 1: Thermophysical Properties of Fluids*, J. V. Sengers, ed., ASME, p. 397 (1982).

Shvarts, A. V., and G. D. Efremova, "Higher-Order Critical Phenomena in the System Ethanol-Water-Carbon Dioxide," *Zh. Fiz. Khim.*, **44**, 1105 (*Russ. J. Phys. Chem.*, **44**, 614).

Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," *Chem. Eng. Sci.*, **27**, 1197 (1972).

Specovius, J., M. A. Leiva, R. L. Scott, and C. M. Knobler, "Tricritical Phenomena in 'Quasi-Binary' Mixtures of Hydrocarbons. 2. Binary Ethane Systems," *J. Phys. Chem.*, **85**, 2313 (1981).

Trebble, M. A., "Calculation of Constants in the Trebble-Bishnoi Equation of State with an Extended Corresponding States Approach," *Fluid Phase Equilib.*, **45**, 165 (1989).

Widom, B., and G. Sundar, "Some Theoretical Aspects of Critical Phenomena in Fluids," *Fluid Phase Equilib.*, **30**, 1 (1986).

Appendix

The "tangent plane distance" function of Eq. 3 has gradient

$$\boldsymbol{g} = \partial F/\partial \boldsymbol{X} \tag{A1}$$

with elements

$$g_i = \partial F/\partial X_i = z_i^{1/2}[\ln f_i(\boldsymbol{n}, V) - \ln f_i(\boldsymbol{z}, V)] \tag{A2}$$

that are accessible without differentiation.

The Hessian of F, $\boldsymbol{B}$, when evaluated for the test phase, has elements

$$B_{ij} = (z_i z_j)^{1/2}(\partial \ln f_i/\partial n_j)_{n=z} \tag{A3}$$

that were found analytically. The differentiation is at constant total volume and temperature.

Evaluation of b and u

In Michelsen and Heidemann (1988), vector $\boldsymbol{u}$ was taken to be the eigenvector of the Hessian, $\boldsymbol{B}$, corresponding to the minimum eigenvalue. Coefficient b in the Taylor series expansion of F then proved to be one-half the minimum eigenvalue. In this work, we have used the approach of Heidemann and Khalil (1980) in determining $\boldsymbol{u}$.

The equation $b = 0$ is in the inner loop of both the "2-D" and the "3-D" calculation procedures examined here. Coefficient b is regarded, in both cases, as a function only of temperature at fixed molar volume and composition. Since b is to be a zero eigenvalue of the Hessian, the Hessian must be a singular matrix with a zero determinant; that is

$$\det(\boldsymbol{B}) = 0 \tag{A4}$$

and vector $\boldsymbol{u}$, is the corresponding eigenvector, satisfying

$$\boldsymbol{Bu} = \boldsymbol{0} \tag{A5}$$

For many systems the determinant of the Hessian is zero at more than one temperature for a given volume. It was found that for all systems investigated in this study, only the high temperature root had any physical significance, the others correspond to unstable phases. The method proposed by Heidemann and Khalil to ensure convergence to the highest temperature root was adopted for use here. With elements given by Eq. A3, $\det(\boldsymbol{B})$ shows a decreasing slope with increasing temperature, making convergence to the upper root difficult. This problem is eliminated by solving

$$\beta = (T/100)^N \det(\boldsymbol{B}) = 0 \tag{A6}$$

for temperature.

In order to evaluate the determinant, the $\boldsymbol{B}$ matrix is first reduced to upper triangular form using Gaussian elimination with scaled partial pivoting (Cheney and Kincaid, 1985, pp. 214-223). The determinant is then the product of the diagonal elements of the reduced matrix, B_{ii}^*:

$$\det(\boldsymbol{B}) = B_{11}^* B_{22}^* B_{33}^* \ldots B_{NN}^* \times (-1)^{n_r} \tag{A7}$$

where n_r is the number of row change operations performed in the Gaussian elimination process. The Newton-Raphson procedure is initiated by setting the temperature 50% higher than the pseudo-critical temperature, and the derivative of $\beta(T)$ with respect to T is obtained using numerical differentiation with central differencing.

The method of Heidemann and Khalil is used also for the calculation of $\boldsymbol{u}$. Using the upper triangular form of $\boldsymbol{B}$, $\boldsymbol{u}$ is determined by setting $u_N = 1$, then, using back substitution, $u_{N-1}, u_{N-2}, \ldots\ldots, u_1$ are calculated. This vector is normalized as follows

$$u_i = u_i \Bigg/ \left(\sum_{j=1}^{N} u_j^2 \right)^{1/2} \qquad \text{(A8)}$$

The $\boldsymbol{u}$ vector constructed in this manner is uniquely determined except for the sign. Because of this property, it is possible that $\boldsymbol{u}$ may become discontinuous. At some points u_N should have a zero value; by initiating the calculation with $u_N = 1$, the intermediate values of u_i become very large and the normalized value of u_N goes to zero. Since u_N is non-negative at all times, the other elements of $\boldsymbol{u}$ change sign when points at which $u_N = 0$ are crossed. This property was not noted in the Heidemann and Khalil (1980) publication, because it does not affect the robustness of ordinary critical point calculations. However, this direction reversal must be eliminated in the calculation of tricritical points.

A simple procedure has been developed to ensure that the eigenvector $\boldsymbol{u}$ does not reverse its direction from one iteration to the next. The procedure may be stated compactly as follows:

$$\text{If} \quad \boldsymbol{u}^{(k)^T} \boldsymbol{u}^{(k-1)} < 0, \quad \text{then} \quad \boldsymbol{u}^{(k)} = -\boldsymbol{u}^{(k)} \qquad \text{(A9)}$$

where $\boldsymbol{u}^{(k)}$ and $\boldsymbol{u}^{(k-1)}$ represent the vector $\boldsymbol{u}$ at the current and previous iterations, respectively.

Evaluation of c and w

Following Michelsen (1984) and Michelsen and Heidemann (1988), an auxiliary vector $\boldsymbol{r}$ is calculated by numerical differentiation, as follows:

$$\boldsymbol{r} = (d^2\boldsymbol{g}/ds^2)_{s=0} \quad \text{with} \quad \boldsymbol{X} = s\boldsymbol{u} \qquad \text{(A10)}$$

The differentiation is performed using a five-point finite difference equation (Abramowitz and Stegun, 1965, Table 25.2). Vector $\boldsymbol{g}$, with elements given by Eq. A2, must be evaluated at five equi-distant points around $s = 0$ ($s = -2h, -h, 0, h, 2h$) where the interval $h = 1 \times 10^{-3}$. For the purposes of numerical differentiation, the composition defined by a given value of s is evaluated from:

$$n_i = s u_i z_i^{1/2} + z_i \qquad \text{(A11)}$$

Given the vectors $\boldsymbol{u}$ and $\boldsymbol{r}$, coefficient c is evaluated from:

$$c = \boldsymbol{u}^T \boldsymbol{r}/3! \qquad \text{(A12)}$$

Vector $\boldsymbol{w}$ that contributes to the compositional variation along the path of minimum tangent plane distance must satisfy the following two equations:

$$\boldsymbol{B}\boldsymbol{w} = 3c\boldsymbol{u} - \boldsymbol{r}/2 \quad \text{and} \quad \boldsymbol{u}^T \boldsymbol{w} = 0 \qquad \text{(A13)}$$

The second of these equations is required since the Hessian, $\boldsymbol{B}$, is singular when $\boldsymbol{w}$ is evaluated.

Evaluation of d, e, and q

Coefficients d and e are obtained by numerical differentiation of the tangent plane distance F. The values depend only on $\boldsymbol{u}$ and $\boldsymbol{w}$; therefore, it is adequate to express mole numbers as a function of s by:

$$n_i = z_i^{1/2}(s u_i + s^2 w_i) + z_i \qquad \text{(A14)}$$

and,

$$dX_i/ds = u_i + 2 w_i s \qquad \text{(A15)}$$

The first derivative of F with respect to s is known analytically; that is,

$$F_s = dF/ds = \sum_{i=1}^{N} g_i (dX_i/ds) \qquad \text{(A16)}$$

It is therefore numerically more effective to determine d and e as follows:

$$4!d = (d^3F_s/ds^3)_{s=0} \qquad \text{(A17)}$$

and

$$5!e = (d^4F_s/ds^4)_{s=0} \qquad \text{(A18)}$$

Higher order terms in the Taylor series for $F(s)$ require knowledge of vector $\boldsymbol{q}$ in the composition expansion. To calculate $\boldsymbol{q}$ requires generation of a further auxiliary vector. This vector is given by;

$$\boldsymbol{p} = (d^3\boldsymbol{g}/ds^3)_{s=0} \quad \text{and} \quad \boldsymbol{X} = s\boldsymbol{u} + s^2\boldsymbol{w} \qquad \text{(A19)}$$

Then, $\boldsymbol{q}$ is calculated from;

$$\boldsymbol{B}\boldsymbol{q} = 4d\boldsymbol{u} - \boldsymbol{p}/6 \quad \text{and} \quad \boldsymbol{u}^T \boldsymbol{q} = \boldsymbol{0} \qquad \text{(A20)}$$

Again, because $\boldsymbol{B}$ is singular, the extra equation is required.

Evaluation of stability coefficient f

Coefficient f is only required to check the local stability of a calculated tricritical point. It is obtained by numerical differentiation of F in a manner analogous to that used in finding coefficients d and e, but in this case,

$$n_i = z_i^{1/2}(s u_i + s^2 w_i + s^3 q_i) + z_i \qquad \text{(A21)}$$

therefore,

$$F_s = \sum_{i=1}^{N} g_i (u_i + 2 s w_i + 3 s^2 q_i) \qquad \text{(A22)}$$

The equation used is,

$$6!f = (d^5F_s/ds^5)_{s=0} \qquad \text{(A23)}$$

A six point differencing scheme must be used, since the 5th derivative is required.

Manuscript received Sept. 25, 1992, and revision received Nov. 23, 1992.