SOME ASPECTS OF MULTIPHASE CALCULATIONS

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ABSTRACT

Computation procedures for locating and constructing phase boundaries in multiphase systems, where a single equation of state is used for calculation of all thermodynamic properties, are described. Special emphasis is given to the calculation of the pressure-temperature bounderies between two-phase and three-phase regions in mixtures of fixed overall composition, and to the calculation of critical points, critical lines and tricritical points.

Introduction

High pressure multiphase equilibria are becoming of increasing interest in connection with processes for enhanced oil recovery. Multiple liquid phases have for example been associated with carbon dioxide injection in low temperature reservoirs (Stalkup, 1983; Orr et al., 1981; Shelton and Yarborough, 1977). In addition multiphase systems have recently been the subject of extensive experimental investigation, (Peng and Robinson, 1985; Hattovy et al., 1981, 1982; Merril et al., 1983). These experimental results will be of great importance in connection with the development and correlation of future thermodynamic models.

The aim of this paper is to describe computational procedures for tracing boundaries of multiphase systems, with particular emphasis on determining three-phase regions, three-phase critical points and tricritical points. The description does not intend to elucidate computational details but rather to provide an overview of the available tools and to explain how established procedures for phase equilibrium calculations can be utilized. It is not our intent to correlate current models with experimental observations, and all model equations are based on simple equations of state of the Van der Waals type, i.e. the SRK-equation (Soave, 1972) and the Peng-Robinson equation (Peng and Robinson, 1976).

Multiphase equilibrium

In the following we shall mainly consider a three-phase N-component mixture of fixed overall composition $\underline{z}$. Mole fractions in phases I, II and III are denoted $\underline{y}$, $\underline{x}$ and $\underline{w}$, respectively, and phase mole fractions for phase I and II by β_1 and β_2.

At equilibrium the following relations must hold

$$\ln y_i + \ln \phi_i(\underline{y}) - \ln w_i - \ln \phi_i(\underline{w}) = 0, \quad i=1,2,\ldots N \tag{1}$$

$$\ln x_i + \ln \phi_i(\underline{x}) - \ln w_i - \ln \phi_i(\underline{w}) = 0, \quad i=1,2,\ldots N \tag{2}$$

in addition to material balance constraints,

$$\beta_1 y_i + \beta_2 x_i + (1-\beta_1-\beta_2) w_i = z_i, \quad i=1,2,\ldots N \tag{3}$$

and the summation of mole fraction constraints,

$$\sum_i y_i = 1 \tag{4}$$

$$\sum_i x_i = 1 \tag{5}$$

i.e. a total of $(3N+2)$ equations $((1)-(5))$ in $(3N+4)$ independent variables $(\underline{x},\underline{y},\underline{w}, \beta_1, \beta_2, T \text{ and } P)$. Thus 2 specifications, not necessarily selected from this set of independent variables, can be selected, and the set of equations is solved for the remaining.

Compared with two-phase calculations numerous additional problems are encountered in solving the set of equations (1-5). At least two phases are dense, which implies that initial estimates based on ideal behaviour are not available. Furthermore, the possibility of near criticality for 3 different phase pairs increases the risk of arriving at "trivial solutions" (with two phases of identical composition). As a result the solution procedure must be chosen with care, and very good initial estimates for the independent variables are usually required. An additional complicating factor is that prediction of conditions where three-phase equilibrium occurs is no trivial problem.

We shall subsequently investigate typical specifications for the phase equilibrium calculation and discuss their respective computational implementations.

"Flash"-specifications

In the abscence of initial estimates the simplest type of calculation is the isothermal flash (specified T and P). A procedure based on the principles outlined by Michelsen (1982a) eliminates the need for a priori knowledge of the

phase distribution at equilibrium. Initially, a single phase of the feed composition is assumed. When the single phase is unstable a two-phase "equilibrium" is established using Gibbs energy minimization (Michelsen, 1982b), and the resulting two-phase distribution (for an unstable initial phase) is subsequently analyzed for stability, with addition of a third phase in the case of instability, etc. No estimates of phase compositions are required, but a fairly extensive amount of trial and error search may be necessary when performing the stability analysis. The use of Gibbs energy minimization in the phase split calculation step is important, since it prevents convergence to "trivial solutions".

The procedure of Michelsen has proven to be fairly reliable. For the mixture shown in Figure 1, the correct phase distribution was determined in the entire temperature and pressure range shown in the figure.
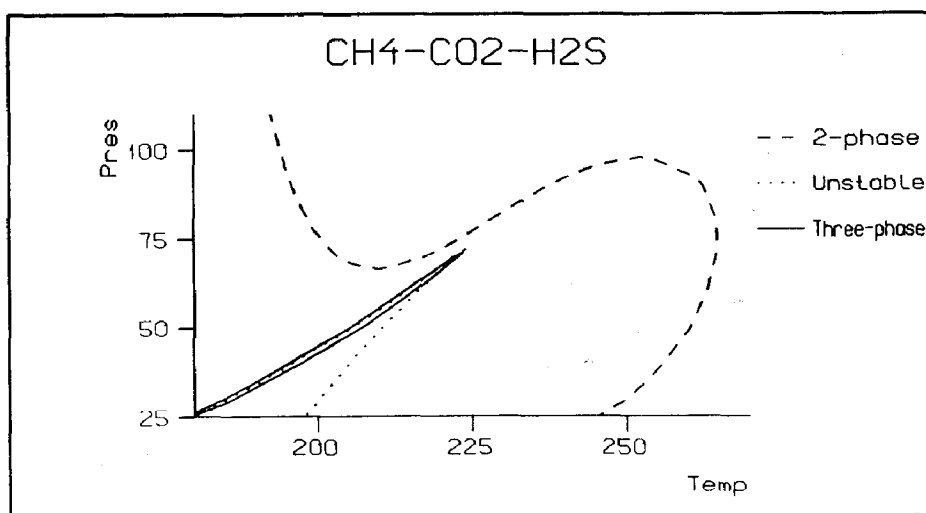

Fig. 1. Phase diagram for mixture containing 70 % CH_4, 10 % CO_2 and 20 % H_2S, using the Peng-Robinson equation of State.

For this particular mixture the three-phase region is rather narrow (at P = 45 atm. from 200.40 K to 202.36 K) and repeated temperature specifications are required in order to locate a point in the three-phase region. Some guidance is obtained from the specifications resulting in 2 equilibrium phases, where high densities of both phases indicate liquid-liquid equilibrium, while a low density phase indicates vapour-liquid equilibrium. The density jump indicates the presence of a three-phase region and can be used to bracket its location, but is is not very helpful in pinpointing the boundaries.

It is often easier to locate a three-phase region, using specifications of pressure and enthalpy (the isenthalpic flash) or pressure and entropy (the isentropic flash), since the three-phase region is "widened" when enthalpy or entropy, rather than temperature is specified. This is evident from the enthalpy-temperature plot for the equilibrium distribution for the mixture of Figure 1 at 45 atm., shown in Figure 2a. The technique used by Michelsen for the isothermal flash can be adapted to the isenthalpic and isentropic case, using minimization of negative entropy, and enthalpy, respectively (Michelsen, 1982 c, 1984a).
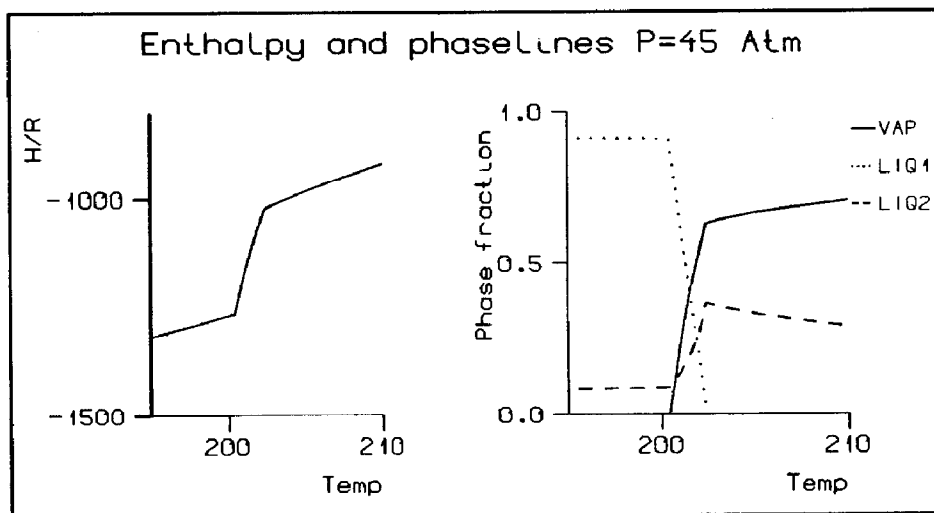

Fig. 2. Temperature-enthalpy diagram for equilibrium composition of mixture of Fig. 1 at P = 45 atm. (a), and Phase distribution for mixture of in dependence of temperature (b).

In flash calculations it is convenient to reduce the number of independent variables by means of the material balance relations. For three-phase calculations only 2N independent variables are required in the isothermal case (i.e. molar flows in two phases, the flows in the third being calculated from the total composition). For the isenthalpic or isentropic flash temperature is an additional independent variable, with the enthalpy- or entropy balance entering as a constraint.

Locating phase boundaries

A problem of particular interest in multiphase equilibrium calculations is that of determining the boundaries of the multiphase region, e.g. by

determining the temperature limits between which three-phases are found at a given pressure. This calculation corresponds to a specification of β_1 (or β_2) equal to zero, in addition to the specification of pressure.

To ensure convergence good initial estimates for all remaining variables are required. Estimates of the required quality can be obtained from repeated flash calculations, followed by a plot of the phase fractions in dependence of temperature or enthalpy in order to locate conditions with one of the three phases present in small amounts. Such a plot for the phase fractions at P = 45 atm. for our example mixture is shown in Figure 2b.

The computationally much simpler tracing of the phase boundary for the two-phase region described by Asselineau et al. (1977) and by Michelsen (1980) may also reveal the existence as well as the location of a three-phase region. Michelsen included in his phase boundary calculation a simple test for intrinsic stability of the "equilibrium phases". Satisfaction of the test does not guarantee stability, but violation of the criterion shows instability. For the mixture of Figure 1, a false "bubble-point" curve can be calculated, as shown on Figure 1. The stability criterion is violated on the entire lower branch, and on the upper branch at pressures above P = 70 atm. The upper part of this branch in practice coincides nearly with the three-phase line corresponding to incipient formation of a vapour phase. The false saturation temperature at P = 45 atm. equals 200.81 K, with the three-phase line located at 200.40 K.

A different situation indicating three-phase behaviour is found in Figure 3 where the two-phase boundary for a mixture of 80% methane, 15% ethane and 5% n-octane is shown. The phase boundary forms a cusp at two points (between these it is intrinsically unstable) and intersects itself. At the point of intersection the overall composition is at equilibrium with two phases of different composition, since the composition of the incipient phase changes continuously along the branch. The point of interception represents a three-phase point ($\beta_1 = \beta_2 = 0$), and an estimate of phase compositions at this point is available from conditions at the point of intersection. A practical problem is that the intersection frequently occurs at a very small angle and hence is difficult to locate. Flash calculations in vicinity of the estimated point of intersection are then required. The region of intersection is shown in detail in Figure 3b, where the three-phase region is also indicated. Isolated three-phase regions of this type tend to be very narrow.
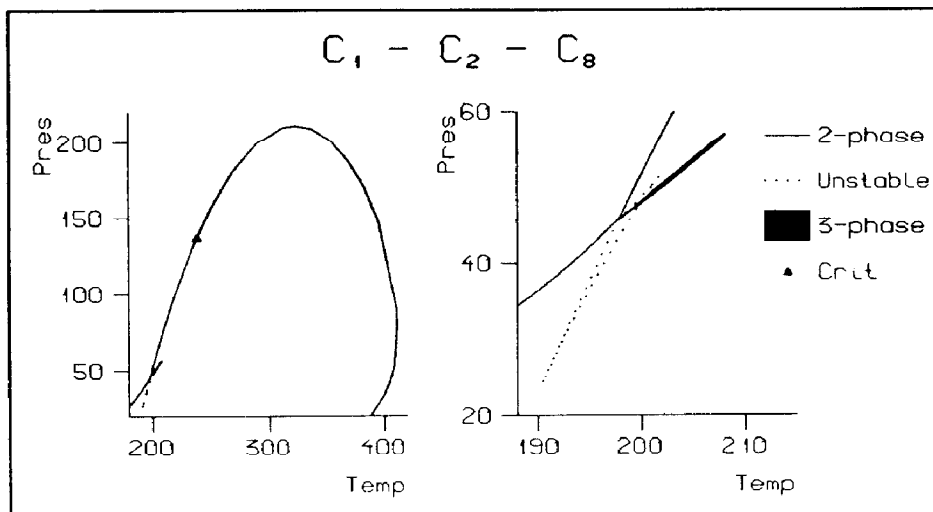
Fig. 3. Phase diagram for mixture containing 80% CH_4, 15% C_2H_6 and 5% $n-C_8$ using the SRK equation of state, and detail of figure showing three-phase region and unstable two-phase line (b).

Calculating phase boundaries

For the actual calculation of three-phase boundaries, a rearrangement of eqns. (1-5) is convenient. Assuming $\beta_1 = 0$ we introduce

$$K_i^{(x)} = x_i/w_i, \qquad K_i^{(y)} = y_i/x_i \tag{6}$$

yielding

$$\ln K_i^{(y)} + \ln \phi_i(\underline{y}) - \ln \phi_i(\underline{x}) = 0 \tag{7}$$

$$\ln K_i^{(x)} + \ln \phi_i(\underline{x}) - \ln \phi_i(\underline{w}) = 0 \tag{8}$$

$$\sum_i y_i - 1 = 0 \tag{9}$$

and

$$\sum_i (x_i - w_i) = 0 \tag{10}$$

where the mole fractions x_i, y_i and w_i are given in terms of β_2 and the equilibrium factors by

$$w_i = z_i/(1-\beta_2 + \beta_2 K_i^{(x)}); \quad x_i = K_i^{(x)} w_i; \quad y_i = K_i^{(y)} x_i \tag{11}$$

The set of (2N+2) equations (6-11) relates 2N+3 variables (the $\ell n\, K_i$, T, P and β_2), and one of these must be specified to perform a calculation of a specific point. Typical specifications comprise T, P or β_2.

When one specific solution to the set of equations (6-11) has been established the phase line can be constructed using a continuation method, as described for the corresponding two-phase problem (Michelsen, 1980). A similar procedure has been used by Li and Nghiem, (1984) who also investigated the case of constant temperature and varying overall composition according to $\underline{z}$ = $(1-\eta)\underline{z}_a + \underline{z}_b$. In contrast to the two-phase boundary automatic tracing of the entire three-phase boundary using internally generated specifications is not easily accomplished. Divergence occurs frequently in the vicinity of critical points, in particular when all equilibrium phases are close in composition. In such situations the Jacobian matrix is severely ill-conditioned, and round-off errors may well prevent the establishment of a converged solution. Some of these problems can be remedied, at the expense of a significant increase in computation time, by the use of quadrupled precision (30 digits) in the calculations.

We therefore prefer to control the phase boundary construction manually, with selection of the specification and the step length after each step. In the case of divergence, repetition with a smaller step length (yielding a better initial estimate) or with a large step (to create distance from a critical point) may both have to be tested.
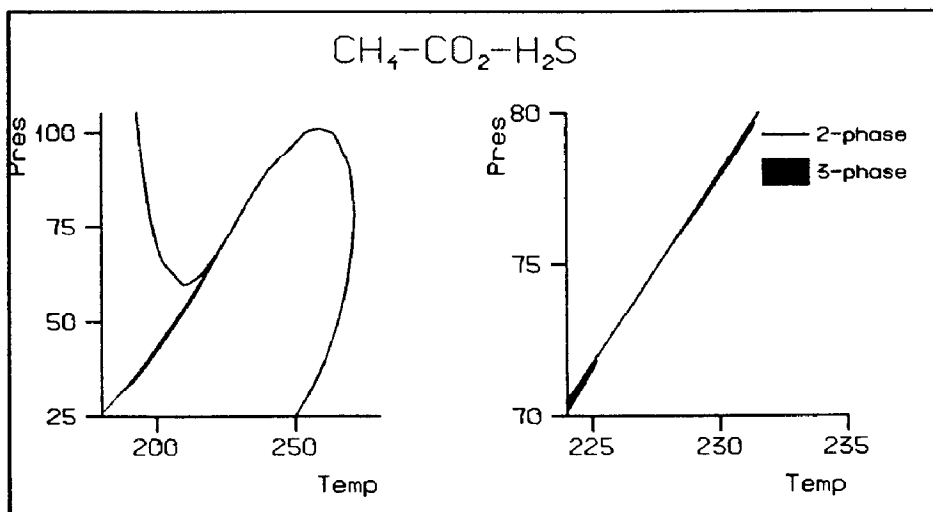

Fig. 4. Phase diagram for mixture containing 64.6 % CH_4, 12.97 % CO_2 and 22.43 % H_2S, using the Peng-Robinson equation of State, and detail of figure showing two separate three-phase regions (b).

An example of complex three-phase behaviour is shown in Figure 4 for a three-component mixture containing 64.6% CH_4, 12.97% CO_2 and 22.43% H_2S, using the Peng-Robinson equation. Construction of the two- phase boundary yields different bubble- and dew lines, that in a certain P-T range run almost parallel, but actually intersect twice, as shown on the tabulation in Table 1. Each point of intersection is a three-phase point, and two disconnected three-phase regions are observed. The isolated high pressure three-phase region is too narrow to show on the plot. Two critical points are found on its phase boundary, for which selected points are presented in Table 2. The other three-phase region extends to low pressures and contains only a single critical point. A slight change in the overall mixture composition cause merging of the three-phase regions, but two separate three-phase points are still found.

TABLE 1

Two-phase "bubble" and "dew"-lines for mixture containing 64.60 % CH_4, 12.97 % CO_2 and 22.43 % G_2S (see Fig. 4), showing two separate intersections.

Pressure (Atm.)	Temperature, Bubble line (K)	Temperature, Dew line (K)
64.	218.58	217.87
66.	220.25	219.94
68.	221.90	221.80
70.	223.54	223.54
72.	225.17	225.20
74.	226.80	226.82
76.	228.41	228.40
78.	230.01	229.97

TABLE 2

The small three-phase region for mixture containing 64.60 % CH_4, 12.97 % CO_2 and 22.43 % H_2S.

Pressure (Atm.)	Temperature, Upper branch (K)	Temperature, Lower branch (K)
75.519	228.021	229.021
77.00	229.217	229.305
78.00	230.027	230.118
79.00	230.844	230.914
79.508	231.266 (Crit)	-
79.265	-	231.119 (Crit)

Critical points

At critical points on the three-phase boundary the incipient phase and one of the two other equilibrium phases are of identical composition. Critical points are most easily located by a construction of the entire phase boundary, using an interpolation technique as described by Michelsen (1980). As mentioned above, however, the equations describing the phase boundary are difficult to converge in the immediate vicinity of critical points, and in addition multiple critical points occur frequently.

An alternative possibility is to apply directly the relations that must hold at a critical point. Assuming that the critical pair is the $\underline{y}$-phase and the $\underline{x}$-phase, these equations can be formulated as follows:

$$\ln K_i^{(x)} + \ln \phi_i(\underline{x}) - \ln \phi_i(\underline{w}) = 0 \tag{12}$$

$$\sum_i (w_i - x_i) = 0 \tag{13}$$

$$b(\underline{x}, T, P) = 0 \tag{14}$$

$$c(\underline{x}, T, P) = 0 \tag{15}$$

with x_i and w_i given in terms of $\underline{z}$, the $\ln K_i^{(x)}$ and β_2 by eqn. (11).

The criticality parameters b and c represent second- and third directional derivatives of the tangent plane distance for the $\underline{x}$-phase, and these are conveniently evaluated as described by Michelsen (1984b)

The first attempt to solve this set of equations was based on nested iterations (Michelsen, 1982b). T and P are assumed, and eqns. (12,13) are solved in an inner loop using an isothermal two-phase flash algorithm. The values of b and c are derived at the resulting $\underline{x}$-phase composition, and temperature and pressure is adjusted in an outer loop to obtain satisfaction of eqns. (14-15). The procedure is convenient, being easy to set up, but not particularly efficient, and very good initial estimates are usually required.

An alternative, which is better suited to tracing critical loci (in dependence of the overall mixture composition) is simultaneous solution of the set of equations (12-15). A drawback of this method is that the composition derivatives of eqns (14-15) must normally be evaluated numerically, and therefore such a method will be expensive when N is large. We shall here briefly describe an alternative method for _ternary_ mixtures.

The simultaneous condition of phase equilibrium and criticality can be expressed as

$$\ln x_i + \ln \phi_i(\underline{x}) - \ln w_i - \ln \phi_i(\underline{w}) = 0 \quad (i=1,2,3) \tag{16}$$

$$b(\underline{x},T,P) = c(\underline{x},T,P) = 0 \hspace{4cm} (17)$$

where the summation of mole fraction constraints are used to eliminate one composition from each phase. Thus, eqns. (16-17) represent 5 equations in 6 variables (x_1,x_2,w_1,w_2,T,P), and the solution can be traced in dependence of one of these variables. Newtons method, with numerical differentiation of eqn. (17) with respect to x_1 and x_2, is used.
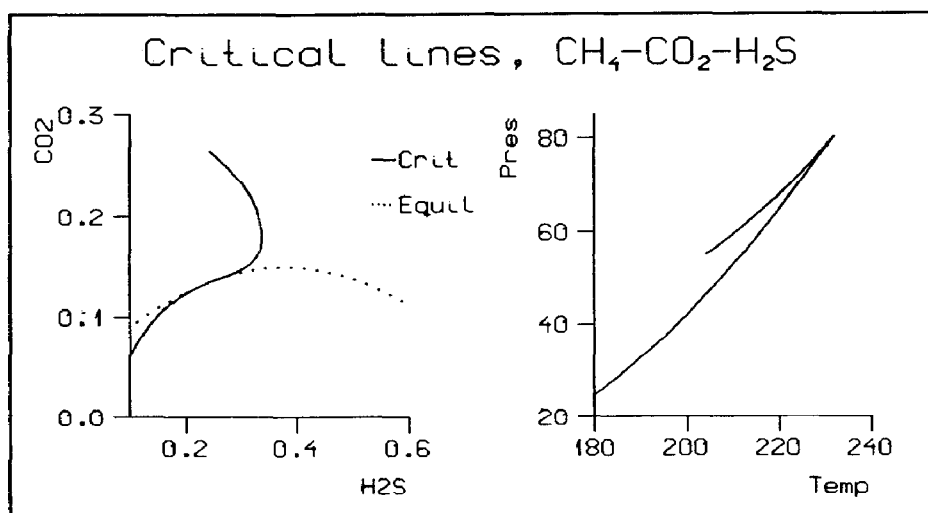

Fig. 5. Critical three-phase lines and equilibrium phase composition for the system CH_4 - $-CO_2$ - $-H_2S$ using the Peng-Robinson equation of State (a), and Pressure-Temperature locus for critical lines (b).

In Figure 5a is presented the locus of critical three-phase compositions for a mixture of methane, carbon dioxide, and hydrogen sulphide, together with the corresponding equilibrium phase compositions. The corresponding pressure-temperature curve is shown in Figure 5b. It is observed that the phase composition curves intersect, and that the P-T curve forms a cusp at the point of intersection. The cross-over point represents the tricritical point for the ternary mixture, i.e. the point where all equilibrium phases are mutually critical.

Tricritical points

The critical locus construction is an indirect method of determining tricritical points. A method for direct calculation based on additional critically parameters d and e (which represent fourth and fifth derivatives of

a tangent plane distance along a parabolic arc in composition space) has also been developed, but will be described elsewhere (Michelsen and Heidemann, 1983).

The calculation of critical three-phase points in the vicinity of the tricritical point is severely affected by round-off errors. A reliable estimate of conditions for tricriticality can however be obtained, observing that the average phase composition defined by $\bar{x}_i = \frac{1}{3}(2x_i + w_i)$ is a much better approximation to the tricritical composition than the individual phase compositions $\underline{x}$ and $\underline{w}$. It can be shown that a difference between $\underline{x}$ and $\underline{w}$ of magnitude ϵ (where ϵ is small) corresponds to a difference between $\bar{x}$ and the tricritical composition of magnitude ϵ^2. In addition T and P deviate from their tricritical values by an amount proportional to ϵ^2.

If we are interested only in locating the mixture tricritical point a computationally as well as conceptually much simpler construction procedure is available. In this procedure, we use the set of 6 equations (1,2) (for a ternary mixture) together with the mole fraction summations to relate 8 variables $(y_1, y_2 x_1, x_2, w_1, w_2, T$ and $P)$.

To complete the specifications, the constraints

$$\ell n\ (y_1/x_1) = \ell n(x_1/w_1) = s \tag{18}$$

where s is specified, are added.

The tricritical point is obtained as the limiting solution for $s \rightarrow 0$. Round-off problems still prevents us from obtaining a solution for very small values of s, but again, $\underline{x}$, T and P deviate only from their tricritical values by an amount proportional to s^2 and hence extrapolation is facilitated.

Two examples of tricritical point construction using eqns. (1,2, 18) are shown in Figure 6 and 7. In both cases we observe the flattening of the three-phase region as $s \rightarrow 0$. In Figure 6 $(C_1-C_2-C_8)$ the triangles converge to a point outside the three-phase region, while Figure 7 $(C_1-C_6-H_2S)$ leads to a tricritical composition inside the three-phase region. The phase diagrams for the respective tricritical compositions, shown in Figure 8 and 9, reflect this difference. For the methane-ethane-octane mixture, no three-phase region is observed, while the tricritical point is located on top of the three-phase region for the methane-hexane-hydrogen sulphide system.

The procedures described above can be extended to handle mixtures containing more than 3 components. Completion of the specification requires N-3 additional constraints, e.g. in the triangle construction by fixing the mole fractions of N-3 components in the $\underline{x}$-phase.
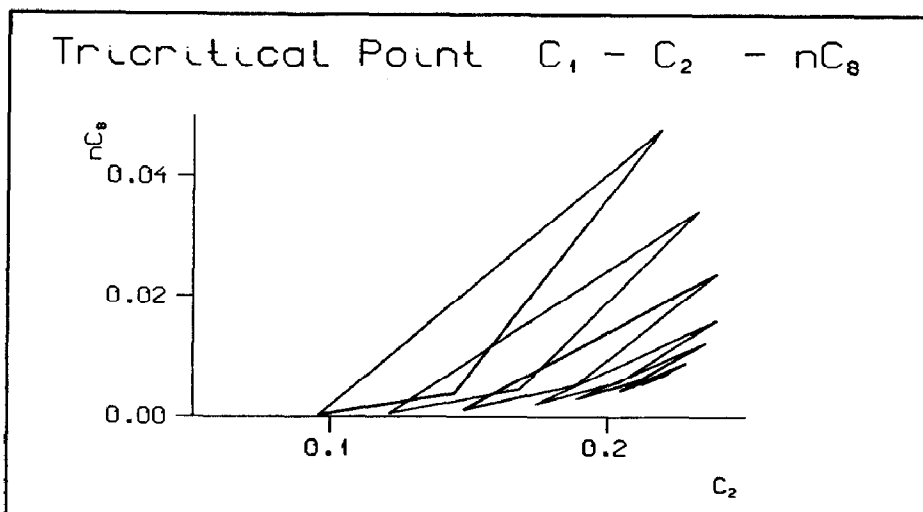
Fig. 6. Triangle construction for Tricritical point determination in the CH_4 - $-C_2H_6$ - $-n-C_8$ system. (SRK-equation).
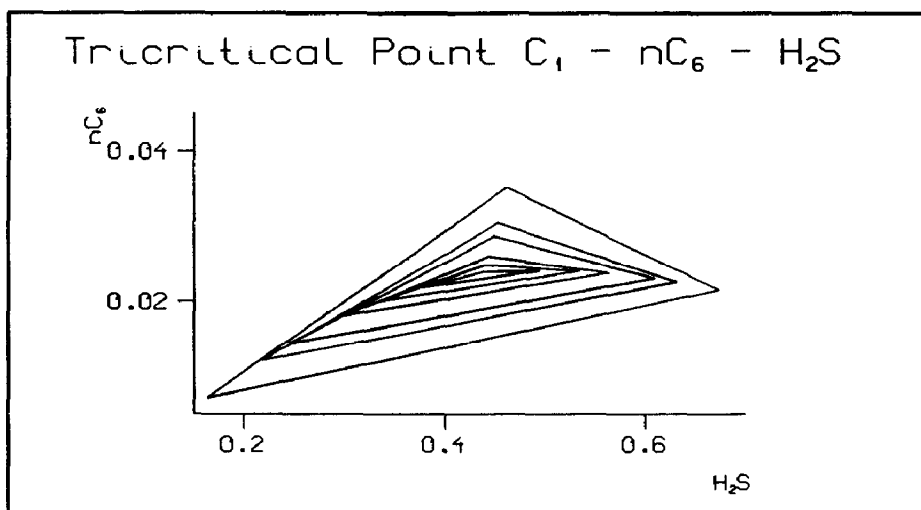

Fig. 7. Triangle construction for Tricritical point determination in the CH_4 - $-n-C_6$ - $-H_2S$ system. (SRK-equation).
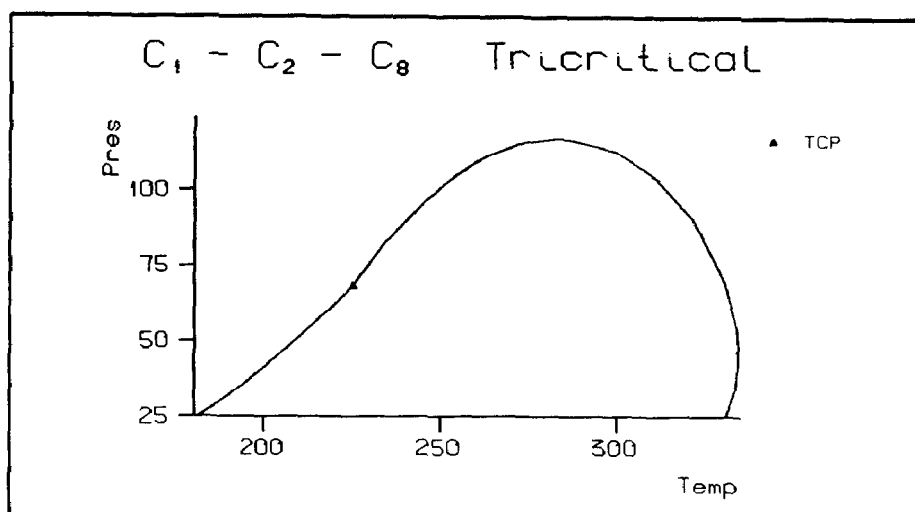
Fig. 8. Phase diagram for mixture of CH_4, C_2H_6 and $n-C_8$ at tricritical composition.
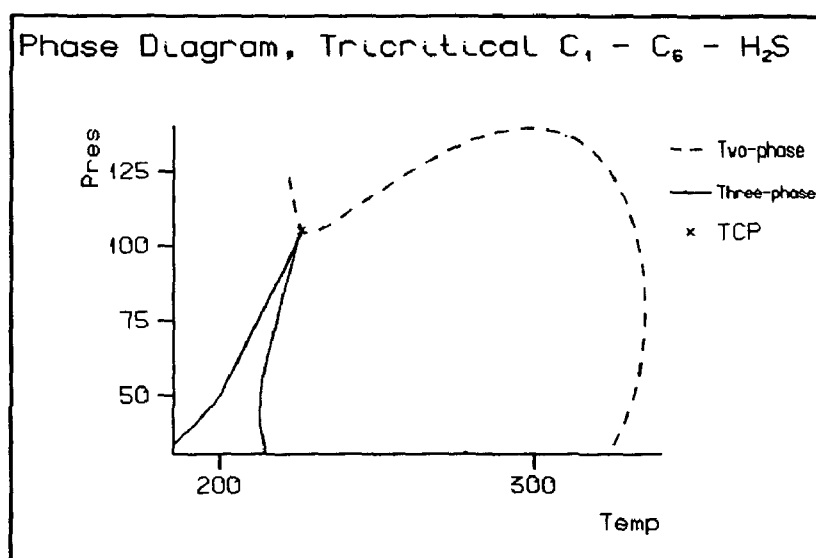

Fig. 9. Phase diagram for mixture of CH_4, $n-C_6$ and H_2S at tricritical composition.

Conclusion

The present paper has described computational procedures for tracing multiphase boundaries and for investigating critical phenomena in multiphase systems. In contrast to two-phase equilibrium the diversity observed in multiphase systems has prevented the construction of procedures capable of fully automatic tracing of multiphase regions, but we believe that the tools described, with proper manual interaction, should enable the mapping of any individual mixture.

Special procedures have been described for tracing three-phase critical loci and for locating tricritical points.

Nomenclature

b	First criticality parameter, eqn. (14)
c	Second criticality parameter, eqn. (15)
i	Component index
K_i	Equilibrium factor, component i
N	Number of components in mixture
P	Pressure (atm.)
s	Distance parameter, eqn. (18)
T	Temperature (K)
w_i	Mole fraction, phase III
x_i	Mole fraction, phase II
y_i	Mole fraction, phase I
z_i	Overall mole fraction, component i

Greek

β_1, β_2	Phase fraction of phase I and II
ϵ	Small quantity
η	Overall composition parameter
ϕ_i	Fugacity coefficient, component i

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