μ = absolute viscosity, μ^*/μ^*_∞
π_1 = $T^*_\infty C^*_2/C^*_1$
π_2 = $C^*_1 C^*_3/C^*_2{}^2$
π_3 = $(C^*_2/C^*_1)\,(\lambda^*/C^*_{PL})$
ρ = density, ρ^*/ρ^*_∞
τ^* = local shear stress at the wall
ψ = stream function

Subscripts

d = liquid drop
g = gas properties
i = interface at liquid/gas boundary layers
L = liquid properties
m = maximum value for impingement on surface
0 = stagnation point
w = condition at wall
∞ = free stream conditions

Superscripts

$'$ = derivative with respect to the independent variable
$^\circ$ = degrees

LITERATURE CITED

Acrivos, A., J. E. Ahearn and A. R. Nagy, "Research Investigation of Two Component Heat Transfer," *ARL Rept. 64-116* (1964).

Bergrun, N. R., "A Method for Numerically Calculating the Area and Distribution of Water Impingement on the Leading Edge of an Airfoil in a Cloud," *NACA TN 1397* (1947).

Brun, R. J., and H. W. Mergler, "Impingement of Water Droplets on a Cylinder in an Incompressible Flow Field and Evaluation of Rotating Multicylinder Method for Measurement of Droplet-Size Distribution, Volume-Median Droplet Size, and Liquid-Water Content in Clouds," *NACA TN 2904* (1953).

Elperin, I. T., "Heat Transfer of Two-Phase Flow with a Bundle of Tubes," *Inzhenero-Fizicheskii Zzhurnal*, 4, 30 (1961).

Goldstein, M. E., W. J. Yang and J. A. Clark, "Boundary Layer Analysis of Two Phase Flow over an Oscillating Flat Plate," *AIAA J.*, 5, 43 (1967).

———, "Momentum and Heat Transfer in Laminar Flow of Gas with Liquid Droplet Suspension over a Circular Cylinder," *J. Heat Transfer*, **89**, 185 (1967).

Goodman, W., "The Evaporative Condenser," *Heating, Piping, and Air Conditioning*, **10**, 165, 255, 327 (1938).

Heyt, J. W., and P. W. Larsen, "Heat Transfer to Binary Mist Flow," *International J. Heat and Mass Transfer*, **14**, 1395 (1971).

Heyt, J. W., and C. C. Lu, "Heat Transfer to Binary Spray Flow with Applied Heat Flux," Southeastern Seminar on Thermal Sciences, Vanderbilt Univ., Nashville, Tenn. (Mar., 1972).

Hodgson, J. W., R. T. Saterbak and J. E. Sunderland, "An Experimental Investigation of Heat Transfer from a Spray Cooled Isothermal Cylinder," *J. Heat Transfer*, **90**, 457 (1966).

Hodgson, J. W., and J. E. Sunderland, "Heat Transfer from a Spray Cooled Isothermal Cylinder," *Ind. Eng. Chem. Fundamentals*, **7**, 567 (1968).

Hoelscher, J. F., Study of Heat Transfer from a Heated Cylinder in Two Phase, Water-Air Flow," M.S. thesis, School of Engineering, Air University, United States Air Force (1965).

Jain, S. C., and J. W. Heyt, "Evaporation and Liquid Film Dry-Out in Binary Spray Flow," 1972 National Heat Transfer Conference, Denver, Colo. (Aug., 1972).

James, B. E., "A Study of Heat Transfer in Unit Refrigerant Condensers Which Use Evaporative Cooling," *J. ASRE*, 169 (1937).

Lu, C. C., "Flow Regime Transition in Binary Spray Flow: Influence of Drop Trajectory," Ph.D. thesis, Univ. Tex., Austin (1972).

Mednick, R. L., and C. P. Colver, "Heat Transfer from a Cylinder in an Air-Water Spray Flow Stream," *AIChE J.*, **15**, 357 (1969).

Schlichting, H., *Boundary Layer Theory*, 4 ed., Translated by J. Kestin, McGraw-Hill, New York (1960).

Smith, J. E., "Heat Transfer Studies of Water-Spray Flows," *ARL Rept.*, 66 (1966).

Takahara, E. W., "Experimental Study of Heat Transfer from a Heated Circular Cylinder in Two-Phase, Water-Air Flow," M.S. thesis, School of Engineering, Air University, United States Air Force (1966).

Thomsen, E. G., "Heat Transfer in an Evaporative Condenser," *Refrigeration Engineering*, 425 (1946).

Thomas, W. C., "Heat Transfer from a Wall Cooled by a Liquid Spray," Ph.D. thesis, Georgia Inst. Technol., Atlanta (1967).

Tifford, A. N., "Exploratory Investigation of Laminar Boundary Layer Heat Transfer Characteristics of Gas-Liquid Spray Systems," *ARL Rept.*, 64-136 (1964).

Wile, D. D., "Evaporative Condenser Performance Factors," *Refrigeration Engineering*, 55 (1950).

Yeh, H. C., and W. J. Yang, "Stagnation Point Forced Convection in Two Phase Flow," *AIAA J.*, 5, 1182 (1967).

Manuscript received June 4, 1979; revision received October 25, and accepted November 7, 1979.

The Calculation of Critical Points

Gibb's classical theory of critical points leads to two simultaneous, nonlinear equations in the intensive variables of the critical phase. In this paper is presented a new procedure for evaluating the functions which appear in these nonlinear equations. The new procedure simplifies and permits the speeding up of the computation of critical points in multicomponent mixtures.

Computations have been performed for critical points in binary and multicomponent mixtures described by the SRK equation. The methods developed will be equally applicable to other two-constant equations of state. The equations to be solved are organized as two equations in the unknown critical temperature and specific volume for a mixture of known composition. One of the two equations, the determinant which establishes the stability limit for the mixture, is shown to be satisfied by more than one volume at a given temperature and by several temperatures at a given volume. A technique is proposed to assure that the correct temperature, volume solution can be found for this equation. For critical points in ordinary gas-liquid systems, an overall computational procedure is suggested in which it proves to be unnecessary to provide initial guesses for either the temperature or the volume.

Application has also been made to several systems with high density (liquid-liquid) critical points.

ROBERT A. HEIDEMANN
and
AHMED M. KHALIL

Department of Chemical Engineering
The University of Calgary
Calgary, Alberta T2N 1N4 Canada

SCOPE

This paper deals with the calculation of critical points in multicomponent mixtures in which all fluid phases are described by an equation of state. Various equations of state are widely used to correlate phase equilibrium in mixtures, particularly mixtures of hydrocarbons. Among these are two constant equations proposed by Wilson (1969), Soave (1972) and Peng and Robinson (1976). Phase equilibrium computation

---

0001-1541-80-2377-0769-$01.25.

procedures are generally poorly behaved in the vicinity of the critical point, and convergence is achieved in this region, if at all, at considerable cost in computational effort. One motivation of the present work is to permit completion of the pressure-temperature diagram for mixtures by locating the critical point through direct computation.

Equations of state are also capable of showing almost all the experimentally observed high density equilibrium phenomena. These include liquid-liquid separations and so-called gas-gas separations of various kinds. Scott and van Konynenburg (1970, 1972) have made an extensive study of the van der Waals equation and have succeeded in showing that the critical behavior of binary mixtures presents a convenient way to classify high density phase separations. Such high density phase separations are important in various applications, including the use of carbon dioxide as a flooding agent in petroleum reservoir operations. A second goal in this study was to develop computational techniques capable of locating liquid-liquid or gas-gas critical points in mixtures described by equations of state.

The theoretical basis for calculating critical points from various kinds of thermodynamic models was laid down by Gibbs (1876). Such calculations were performed for binary systems using equations of state even by van der Waals, but the extension to ternary systems was first made by Spear et al (1971), and applications to larger systems are so far represented only by the work of Peng and Robinson (1977) and Baker and Luks (1978). The critical conditions reduce to finding the zeroes of two nonlinear functions of the intensive variables in the critical phase, but these functions are of such complexity as to discourage application to large systems (Spencer et al., 1973). In the standard approach, as employed by Peng and Robinson, it is necessary to find (N^2-2N+3) determinants of order (N − 1) at each test point merely to evaluate the functions. In this paper we have taken a new look at the mathematics of the critical point and have found an alternative way to evaluate the two functions which reduces the amount of computation markedly, making possible applications to very large systems.

CONCLUSIONS AND SIGNIFICANCE

The paper presents a new statement of the critical point criteria for multicomponent mixtures described by equations of state; that is, the quadratic and cubic form in the expansion of the Helmholz free energy as a function of the mole numbers are both zero, for some variation $\Delta\bar{n}$, at a critical point. The second of these functions, the cubic form, is evaluated with much less computational effort than the determinant usually employed in its place.

A computational algorithm has been developed, based on the new critical point criteria, that converged to the critical temperature and volume (whenever the system in question had a vapor-liquid critical point) for all systems studied, with a single strategy for making the initial guess.

It is demonstrated also that liquid-liquid phase separations can be anticipated in a given system by examining the stability limit. In systems without any liquid-liquid separations, as the density increases, the pressure along the stability limit tends toward negative infinity. However, in some systems, pressure along the stability limit remains positive at high density, indicating a region of positive temperature and pressure in which the high density fluid is unstable. Any critical point, whether characterized as a liquid-liquid or vapor-liquid critical point, can be found by searching along the stability limit. Systems are described in which three critical points and no critical points are found on the stability limit.

The basis for any theory of critical points was established by Gibbs (1876) who showed that a critical phase must obey two restrictions and presented several different forms for expressing these conditions, depending upon which of the thermodynamic variables were considered to be independent. The form of the critical conditions most frequently cited results from considering the pressure and temperature and mole fractions as independent variables. These are the conditions employed by Peng and Robinson (1976) in their study of critical points in large systems. Reid and Beegle (1977) have used Legendre transforms to explore the variety of forms the critical conditions can take.[The papers by Peng and Robinson (1977) and Reid and Beegle (1977) both contain extensive accounts of previous critical point computations.]

The variables most convenient to consider as independent when we deal with pressure explicit equations of state are the temperature, the volume and the mole numbers or mole fractions. With these independent variables, the critical point conditions are expressed as properties of the Helmholz free energy function. Baker and Luks (1978) use this sort of formulation.

In this paper we propose a new way of expressing the critical point criteria. The starting point taken in the development of these criteria is, of course, to be found in Gibbs (1876).

STABILITY

Critical criteria are found by examining the stability of homogeneous phases. A given phase held at conditions (T_0, V_0, n_{10}, n_{20}, . . . , n_{N0}) will be stable if for every isothermal variation in the state, the new state being (T_0, V, n_1, n_2, . . . , n_N)

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

In (1), the pressure P_0 and the chemical potentials μ_{i_0} are all evaluated at the test point (the initial state), and $A - A_0$ is the difference in Helmholtz free energy between the varied and the initial state.

A second condition must be satified for nonisothermal variations; that is

$$[A - A_0 + S_0(T - T_0)]_{V_{0,n_{j0}}} > 0 \qquad (2)$$

This second condition is satisfied so long as the heat capacity at constant volume is positive and is not of primary concern in the development which follows.

Equations (1) and (2) are equivalent to Equations (153) and (154) in Gibbs (1876). If these two inequalities are not satisfied for any change in phase in a region around the test point, there is a lower internal energy accessible to the mixture by separating into two or more phases.

A variation of the kind

$$\Delta V = kV_0$$
$$\Delta n_i = kn_{i0},\ i = 1, \ldots, N \qquad (3)$$

does not qualify as a change in phase; the mole fractions and density, hence the pressure and chemical potentials, will be constant under such a variation. To eliminate this possiblity, we set

$$\Delta V = 0 \qquad (4)$$

thus reducing (1) to

$$\left[A - A_0 - \sum_{i=1}^{N} \mu_{i0}\,\Delta n_i\right]_{T_0,\,V_0} > 0 \qquad (5)$$

The Helmholtz free energy can be expanded in a Taylor series around the test point, giving

$$\left[A - A_0 - \sum_{i=1}^{N} \mu_{i0}\Delta n_i\right]_{T_0,\,V_0} = \frac{1}{2!}\sum_j\sum_i (\partial^2 A/\partial n_j\partial n_i)\,\Delta n_i\Delta n_j$$
$$+\frac{1}{3!}\sum_k\sum_j\sum_i (\partial^3 A/\partial n_k\partial n_j\partial n_i)\Delta n_i\Delta n_j\Delta n_k + 0\,(\Delta n^4) \qquad (6)$$

Stability of the test point requires that this quantity should be positive for all arbitrary Δn.

The Limit of Stability

Stability is assured if the quadratic form in Equation (6) is positive-definite. At test points (T_0, V_0, n_{10}, . . . , n_{N0}) on the limit of stability, the quadratic form is positive-semidefinite. At such points, stability is determined by the properties of the cubic form and the higher-order terms.

A necessary condition for a point to lie on the limit of stability is that the matrix Q with elements

$$q_{ij} = \left(\frac{\partial^2 A}{\partial n_j \partial n_i}\right) \qquad (7)$$

should have a zero determinant:

$$Q = Det(\mathbf{Q}) = 0 \qquad (8)$$

Or equivalently, there should be a vector

$$\overline{\Delta n} = (\Delta n_1, \Delta n_2, \ldots, \Delta n_N)^T$$

which satisfies the equations

$$\mathbf{Q} \cdot \overline{\Delta n} = 0 \qquad (9)$$

Such a point may be unstable, since the determinants of all the principal minors of Q must be non-negative if Q (hence the quadratic form) is to be positive-semidefinite. However, at every point on the limit of stability, Equations (8) and (9) must hold.

The vector $\overline{\Delta n}$ which satisfies Equation (9) is unique within a scalar multiple (except, possibly, at isolated points where the rank of Q is less than $N - 1$). This is a familiar result of linear algebra.

CRITICAL POINTS

The definition which we employ for a critical point is that proposed by Reid and Beegle (1977). We say that a critical point is a stable point which lies on the stability limit. This definition requires that the quadratic form in (6) should be positive-semidefinite, hence that a vector $\overline{\Delta n}$ satisfying (9) can be found, and also that when this $\overline{\Delta n}$ is inserted in (6), the first nonvanishing term in the Taylor series must be of even order. In particular, the cubic form must vanish

$$C = \sum_k\sum_j\sum_i \left(\frac{\partial^3 A}{\partial n_k \partial n_j \partial n_i}\right)\Delta n_i\Delta n_j\Delta n_k = 0 \qquad (10)$$

for $\overline{\Delta n}$ satisfying (9).

Equations (8), (9) and (10) lead directly to a procedure for calculating critical points. While this procedure may appear unlike the usual procedure of setting two determinants equal to zero, the results are equivalent. The two conditions for a critical point, in this case, are Equations (8) and (10), with the Δn_i in Equation (10) to be found from Equation (9).

Beegle et al. (1974*a*, 1974*b*) and Reid and Beegle (1977), using Legendre transforms, have shown that the criteria for the stability limit and the critical point can be expressed in many equivalent forms, depending on the choice and ordering of the independent variables. Our Equations (8), (9) and (10) correspond to one specific choice of independent variables.

The step of taking $\Delta V = 0$ [Equation (4)] has the effect of producing symmetrical quadratic and cubic forms. Perfectly equivalent results are obtained by setting $\Delta n_k = 0$, where k is the index of any one of the mixture components. If this is done, however, the quadratic and cubic forms will involve derivatives of pressure, and the symmetry will be lost.

APPLICATION TO EQUATIONS OF STATE

In this study, calculations have been limited to the Soave modification of the Redlich-Kwong equation (Soave, 1972). The methods are expected to be equally applicable to other pressure-explicit equations of state. The fugacities are found as

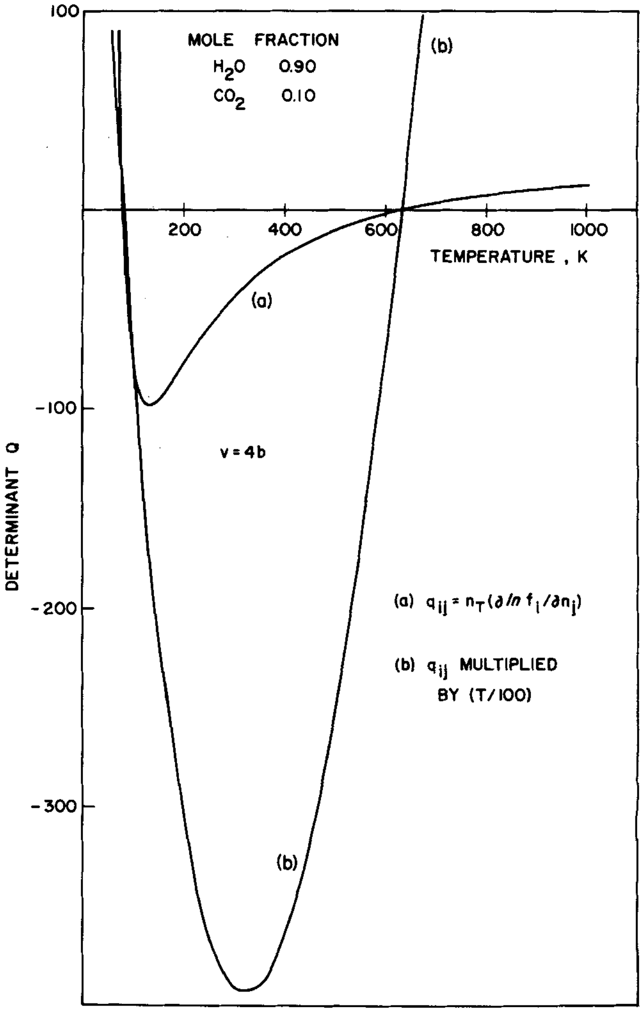

Figure 1. Determinant Q as a function of temperature at v = 4b, showing two points Q = 0.

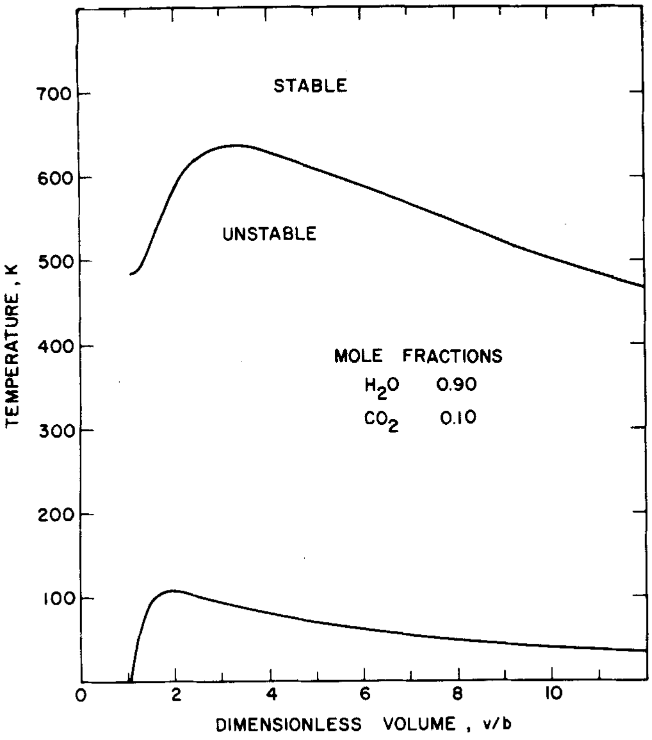

Figure 2. Temperature-volume boundaries of the unstable region.

functions of temperature, volume and mole numbers using standard thermodynamic identities. Then the elements in the quadratic and cubic forms of the critical criteria are found from

$$(\partial^2 A/\partial n_j \partial n_i) = RT\,(\partial \ln f_i/\partial n_j) \qquad (11)$$

and

$$(\partial^3 A/\partial n_k \partial n_j \partial n_i) = RT\,(\partial^2 \ln f_i/\partial n_k \partial n_j). \qquad (12)$$

One consideration which helps to reduce computational effort is that the same result is obtained in Equations (11) and (12), whatever is the order of differentiation. Then

$$(\partial \ln f_i/\partial n_j) = (\partial \ln f_j/\partial n_i) \qquad (13)$$

and

$$(\partial^2 \ln f_i/\partial n_k \partial n_j) = (\partial^2 \ln f_j/\partial n_k \partial n_i) = (\partial^2 \ln f_k/\partial n_j \partial n_i) \qquad (14)$$

These derivatives, for the SRK equation, are given in the Appendix.

Evaluating the Stability Limit

To find a point on the stability limit for a mixture of given composition requires finding a temperature, volume pair which makes the determinant Q equal to zero. This proved to be a more complex problem than might at first be anticipated. We soon discovered that, for most systems, there was more than one volume that satisfied $Q = 0$ for given temperature and that, for some systems, $Q = 0$ at more than one temperature for a given volume.

Figure 1 demonstrates the second of these points. The figure is for a mixture with 10 mole % carbon dioxide in water. The volume is taken to be 4b. Curve (a) is the determinant of the 2 × 2 matrix with elements

$$q_{ij} = n_T\,(\partial \ln f_i/\partial n_j) \qquad (15)$$

Zeroes of this determinant are also zeroes of the quadratic form in Equation (7), but there is the advantage in (15) that these q_{ij} are dimensionless. The two zeroes, one near 630K and one near 80°K, are evident in Figure 1.

Figure 2 shows two (T, v) curves which satisfy $Q = 0$; at each volume there are two temperatures. It will be noticed also that along each of the two curves there are points corresponding to the same temperature but with different values for the volume.

In Figure 2 it is certain that, at every volume, when the temperature is raised high enough the phase becomes stable. The low temperature curve is not of any interest in this mixture, since the temperatures are everywhere below 120°K.

It was felt necessary to develop a technique that would converge in every case to the highest temperature at which the stability limit was reached for a given volume. Curve (a) in Figure 1 shows a decreasing slope as temperature increases, caused by the dominance of terms in 1/T in the derivatives of Equation (15). It is difficult to assure convergence to the high temperature root of $Q = 0$ with this shape. This difficulty is eliminated by taking

$$q_{ij} = (T/100)\, n_T\,(\partial \ln f_i/\partial n_j) \qquad (16)$$

which is also dimensionless (if the 100 is taken to have units of kelvins). The determinant with elements given by (16) has the properties of a polynomial in T of order N; for high T this determinant shows an increasing slope, as given by curve (b) in Figure 1.

The relatively small step of using (16) to define elements in the quadratic form removes much of the difficulty in finding the stability limits. For every volume, if the initial temperature is taken large enough, the Newton-Raphson procedure converges monotonically to the highest temperature on the stability limit.

The determinant of the quadratic form Q is evaluated, in our routine, by first using Gaussian elimination with column pivoting (Burden et al., 1978, page 340) to reduce the $\mathbf{Q}$ matrix to upper triangular form; then Q is the product of the diagonal elements.

At each volume, the temperature is found by the Newton-Raphson procedure, with numerical differentiation to obtain $\partial Q/\partial T$. In the numerical differentiation we take

$$dT/T = 1 \times 10^{-5} \qquad (17)$$

and the criterion of convergence is that between successive iterations

$$|\Delta T|/T \leq 1 \times 10^{-4} \qquad (18)$$

To converge to the correct temperature, it is only necessary to make the initial guess high enough. The guess we use is

$$T = 1.5 \sum_i y_i T_{c_i} \qquad (19)$$

With this initial guess, it was always possible to find the highest T on the stability limit for a given volume.

Evaluation of $\overline{\Delta n}$

The upper triangular matrix produced in evaluating Q is used to find $\overline{\Delta n}$. We first take $\Delta n_N = 1$, then use back substitution, using the reduced form of Q, to find Δn_1, Δn_2, . . . etc. It proved to be important to scale Δn by dividing by

$$D \equiv \left[\sum_{i=1}^{N} (\Delta n_i)^2\right]^{1/2} \qquad (20)$$

The $\overline{\Delta n}$ vector constructed this way is uniquely determined at points where $Q = 0$, except for the sign. An equally useful $\overline{\Delta n}$ could be found by beginning with $\Delta n_N = -1$.

One concern which developed in solving for critical points was that $\overline{\Delta n}$ can become discontinuous. In reducing Q to upper triangular form, the pivoting algorithm has the effect of changing the sequence of equations. Unless $Q = 0$, the $\overline{\Delta n}$ vector may depend on which equations are solved. In our case, we solved for $\overline{\Delta n}$ only at points where $Q = 0$.

There is a second way in which $\overline{\Delta n}$ becomes discontinuous. At some points, Δn_N should be zero. We begin always with $\Delta n_N = 1$

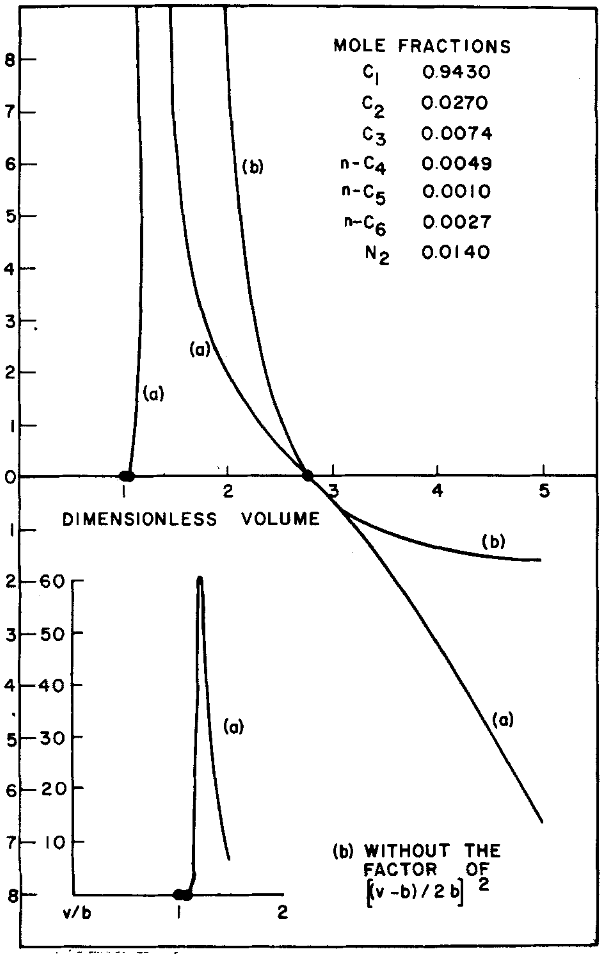

Figure 3. The cubic form, C, in a seven component system.

and then normalize. In this procedure the intermediate values of the Δn_i become very large so that the normalized value of Δn_N is reduced to zero. However, since Δn_N is always non-negative in this procedure, the other elements of $\underline{\Delta n}$ change sign as points where $\Delta n_N = 0$ are crossed.

Evaluation of the Cubic Form

In the place of the cubic form of Equation (10), we evaluate

$$C = [(v-b)/2b]^2 \sum_{k=j}^{N} \sum_{j=i}^{N} \sum_{i=1}^{N} h_{ijk} n_T^2 (\partial^2 \ln f_i/\partial n_k \partial n_j) \Delta n_i \Delta n_j \Delta n_k \tag{21}$$

where

$$h_{ijk} = \begin{cases} 1; \; i = j = k \\ 3; \; i = j \neq k, \; i = k \neq j, \; j = k \neq i \\ 6; \; i \neq j \neq k, \; i \neq k. \end{cases} \tag{22}$$

The factor h_{ijk} accounts for the number of identical terms in the cubic form; its inclusion permits reduction of the number of terms to be summed from N^3 to $N(N+1)(N+2)/6$.

In our calculation procedure, the temperature on the stability limit was found at each volume. Then the Δn_i were found. The cubic form (21) was then evaluated.

Figure 3 shows a typical shape of the cubic form, in this case for a seven-component system. The two curves show Equation (21) with and without the multiplying factor $[(v-b)/2b]^2$. In this figure there are three volumes at which the cubic form becomes zero, all of which must be considered possible critical points.

For a vapor-liquid critical point, the volume which is of interest is the largest volume; the higher density solutions to the critical point criteria, if they have meaning, would apply to liquid-liquid separations. When the cubic form of Equation (21) is used, including the multiplying factor $[(v-b)/2b]^2$, convergence to the vapor-liquid critical point is assured (whenever the mixture has such a critical point) by taking a large volume as the initial guess. With this factor, the cubic form has the shape of a quadratic in volume at large volumes. The Newton-Raphson procedure converges monotonically to the critical volume from an initial guess of

$$v = 4b \tag{23}$$

For pure components, the Redlich-Kwong equation and its variants have

$$v_c = 3.85\, b \tag{24}$$

The critical volumes of mixtures are always less than this value.

In the seven-component system for which Figure 3 is drawn, potential critical points (where $C = 0$) at low volumes corresponded to negative pressures and can be ignored. Nonetheless, the existence of these roots to the critical point equations potentially can create difficulties with the numerical procedures.

The procedure we employed proved to be quite robust. The initial volume guess is $v = 4b$, as in Equation (23). At this volume the temperature at which $Q = 0$ is found, as described above, with an initial guess of Equation (19). In all following calculations, the last obtained value of the temperature is used as the initial guess.

The derivative of the cubic form with respect to the volume is found numerically with

$$dv/v = 1 \times 10^{-5} \tag{25}$$

At v and $v + dv$, the corresponding temperatures and the Δn_i have to be determined before the cubic form can be evaluated.

The convergence criterion employed is

$$|\Delta v|/v < 1 \times 10^{-4} \tag{26}$$

in successive iterations.

This procedure, consisting as it does of nested one-dimensional searches, may appear inefficient. However, it has the feature that convergence is assured with a single strategy for the initial temperature and volume guesses for all vapor-liquid critical points.

VAPOR-LIQUID CRITICAL POINTS

The computational scheme described above was used to calculate critical points in a number of multicomponent mixtures including all thirty-two systems documented by Peng and Robinson (1976). In all cases where a conventional vapor-liquid critical point exists, the procedure converged in three to five iterations with the initial guess for temperature and volume of Equations (19) and (23), respectively.

The computer used was the CDC Cyber 172 at the University of Calgary. Computation times on this machine are correlated roughly by

$$t = N^2(0.035 + 0.00022\, i\, N) \tag{27}$$

In order to test the limitations of the procedure, we attempted computations on systems containing fifteen, twenty and, finally, forty-three components. The forty-three-component mixture studied had the composition of the crude oil produced in Alberta's Swan Hills reservoir. The compositional data were obtained from Yu (1975).

In none of these large systems was any computational difficulty encountered. Convergence was obtained to the precision indicated in Equations (18) and (26) in four or five iterations. For the forty-three-component system, the computational time was 152 s.

We also calculated the critical line for one binary system with an azeotrope, carbon dioxide ethane. Teja and Rowlinson (1973), in their computations of critical points in binary and ternary systems, encountered numerical difficulties in the com-

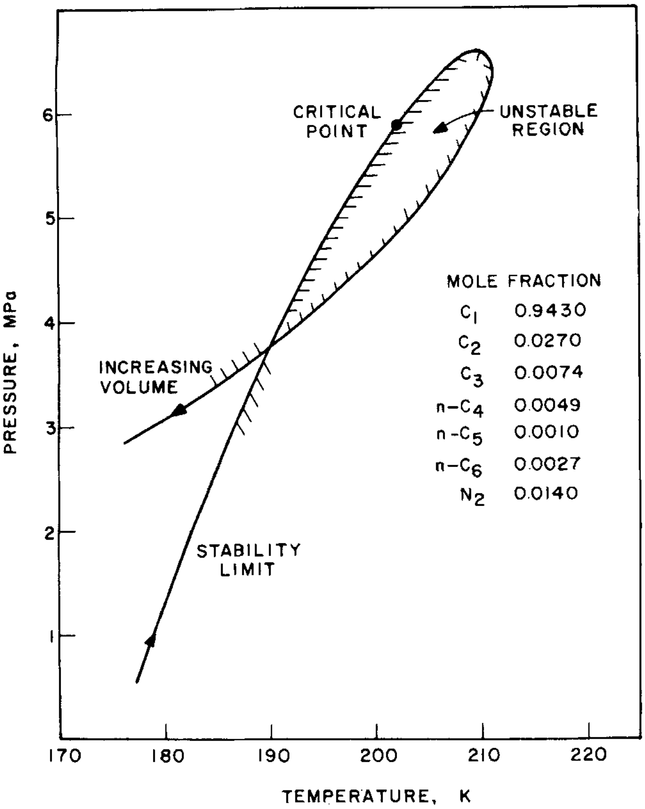

Figure 4. Stability limits on the P-T plane, for a seven component system.

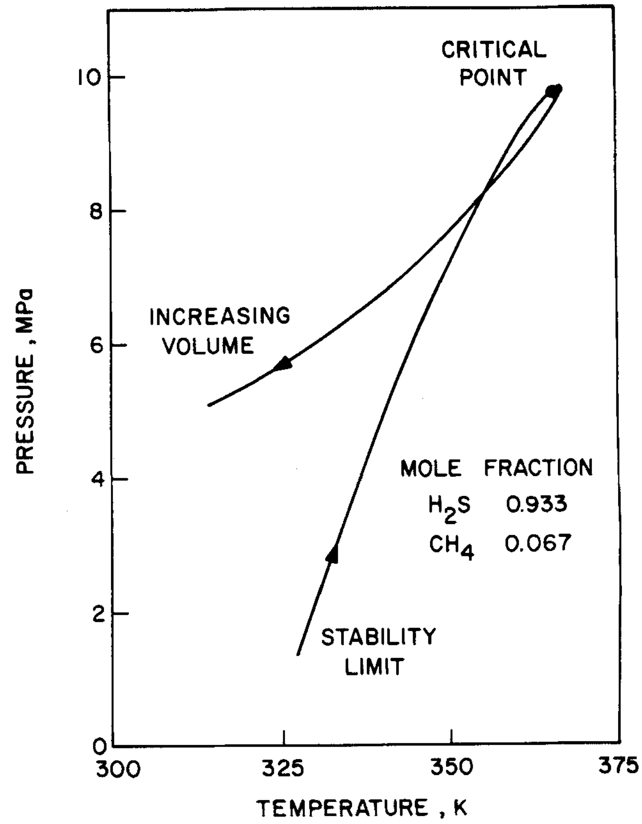

Figure 5. Stability limit for a CH_4–H_2S mixture rich in CH_4.

position region where the azeotropic line intersects the critical line for carbon dioxide-ethane. In a later publication, Teja and Kropholler (1975) described a technique to overcome the difficulty. In our procedure, there was no complication of any kind encountered because of azeotropy in this system.

For vapor-liquid equilibrium points, the present calculation procedure differs from the Peng and Robinson (1977) procedure in several ways. In our formulation, to evaluate the second of the two critical criteria requires solving a set of simultaneous equations and inserting the result in the cubic form, Equation (21). In the usual formulation, as used by Peng and Robinson (1977), the equivalent step involves evaluating $N^2 - 2N + 3$ determinants of order $N - 1$.

Baker and Luks (1978) use the Helmholtz free energy to obtain critical point criteria, as we do. However, their procedure requires evaluation of pressure derivatives, which we avoid. Also, the second critical point equation used by Baker and Luks requires evaluation of a large number of determinants, just as in the calculations of Peng and Robinson (1977). Our procedure evades the extensive bookkeeping involved in programming this step.

Baker and Luks also report calculations in which the critical temperature is specified and a search is performed for one mole number and the pressure corresponding to a critical phase. Calculations of this kind are of interest in certain petroleum recovery operations. Our procedure has not been adapted to attack problems of this kind.

We also have proposed an algorithm which removes the need to supply an initial guess for the critical temperature and volume (or pressure). Because the nonlinear equations to be solved can have several solutions, a poor initial guess can cause the computations to fail. In a two-dimensional Newton-Raphson procedure, as used by Peng and Robinson (1977), the initial guess has to be made wisely in order to obtain convergence.

The accuracy obtained in the predictions of critical temperature and pressure are comparable in this study (using the SRK equation) with the Peng-Robinson results. Critical volumes from the SRK equation are always too large, owing to the limitation that $Z_c = 1/3$, and errors on the order of 20 to 30% occur. Peng and Robinson (1977) report smaller errors with their equation.

The calculation procedure described here is equally applicable to any two-constant equation of state. The accuracy of the predicted critical properties is not a major concern in this work, except to the extent that the accuracy is sufficient to justify the calculations. If more accurate critical properties are predicted

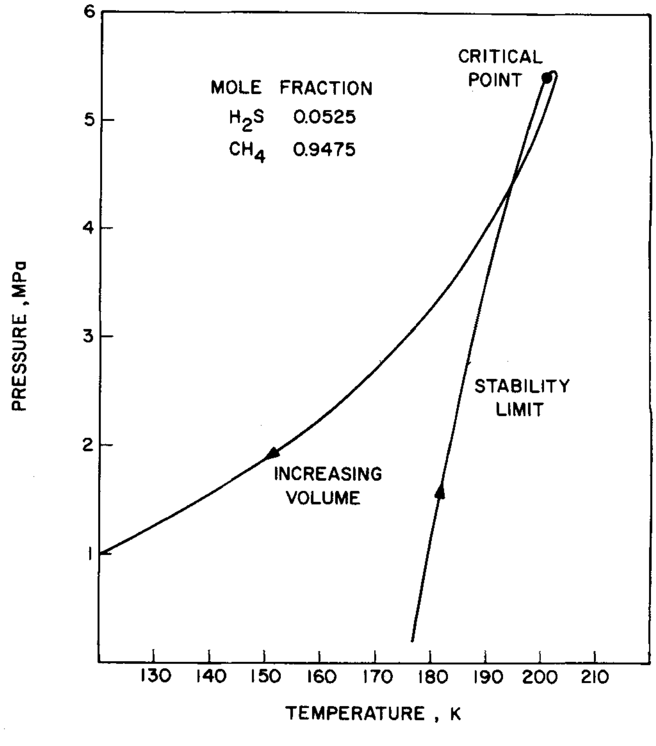

Figure 6. Stability limit for a CH_4–H_2S mixture rich in H_2S.

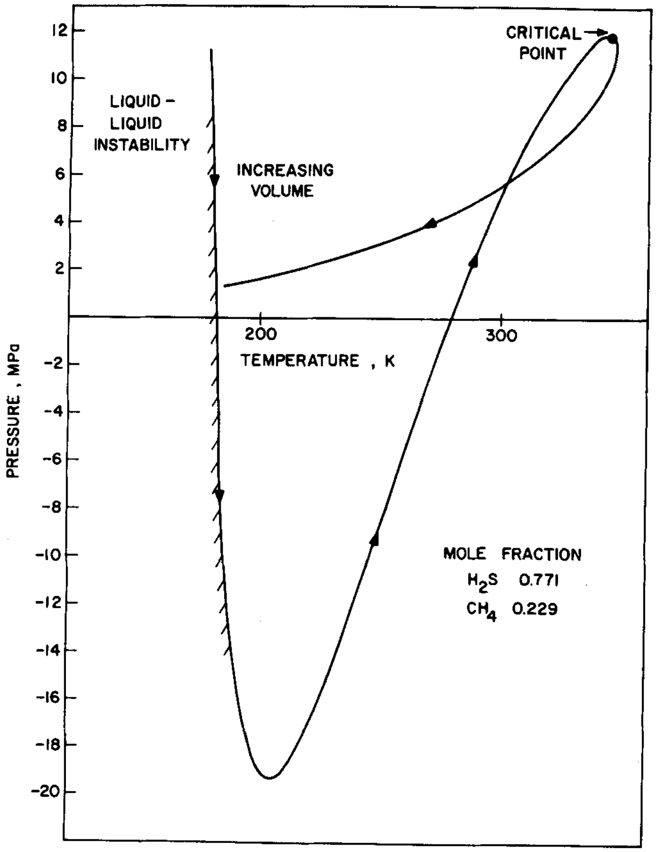

Figure 7. Stability limits in a mixture with liquid-liquid phase separations.

by some other equation of state than the SRK equation, the proposed calculation procedure should be of use in finding them.

The accuracy also depends on the values used for interaction parameters in equations of state. Deiters and Schneider (1976) have shown that interaction parameters fitted by matching critical data can be employed in vapor-liquid equilibrium calculations.

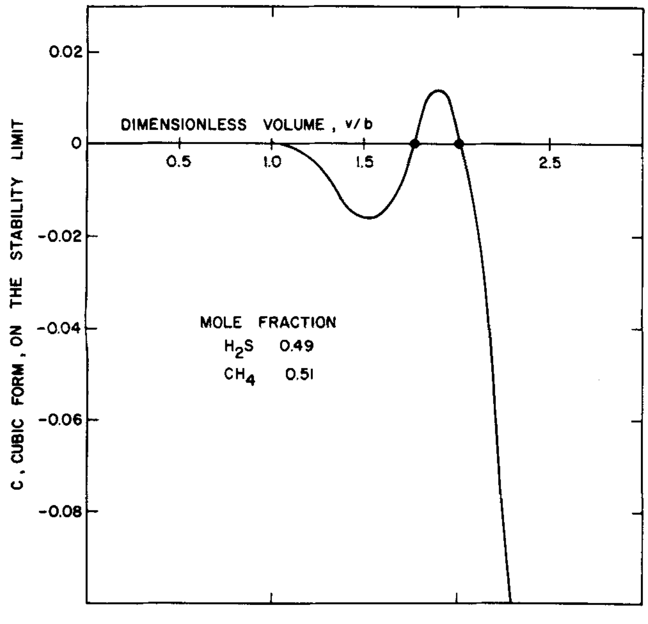

Figure 9. The cubic form for the mixture of Figure 8, showing two critical points.

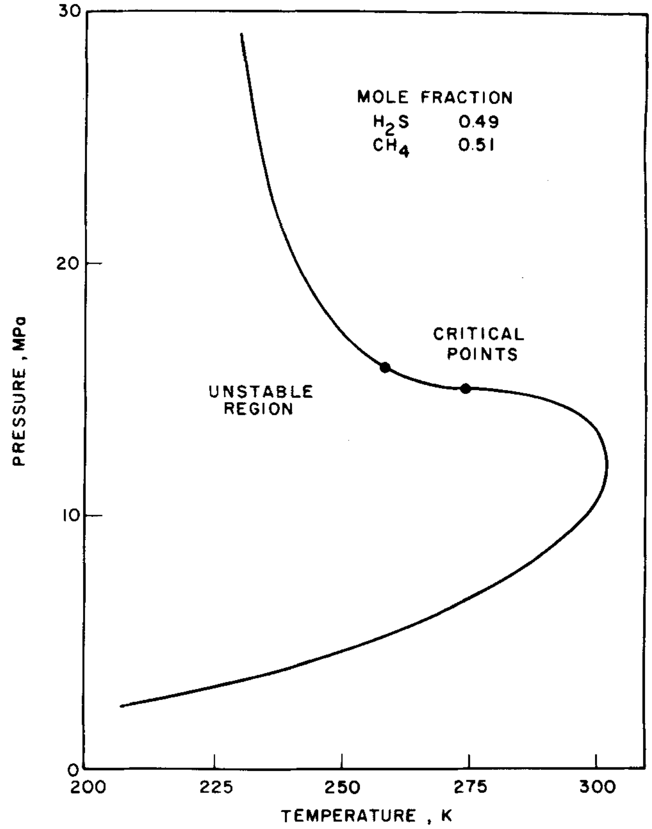

Figure 8. Stability limit for a CH_4-H_2S mixture with two calculated critical points.

LIQUID-LIQUID SEPARATIONS

In systems where liquid-liquid separations can occur, there may be no critical point, or more than one. As part of this study we developed some techniques to identify systems which may show liquid-liquid instability and to locate all possible critical points in such systems.

The Stability Limit

Figure 4 shows the temperature-pressure projection of the stability limit in a seven-component system (the same system as in Figure 3). At each volume the highest temperature is found for which the determinant Q is zero; then the pressure is calculated at the temperature and volume. The direction of increasing volume is shown on the stability limit curve.

The coexistence region is tangent to the stability limit at the critical point and contains the unstable region. We have not drawn the boundary of the coexistence region in any of the figures following.

Figures 5 and 6 show similar stability limit curves for hydrogen sulfide-methane mixtures, one rich in hydrogen sulfide and one rich in methane. For pure substances, the loop at the top of these curves degenerates to a cusp with the critical point at the cusp. In general, the high volume extension of the stability limit curve represents the limit of subcooling of the vapor, and similarly the low volume extension gives the limit of super heating of the liquid.

In Figures 4, 5 and 6, as the volume decreases toward $v = b$, the pressure becomes negative along the stability limit. This is typical of vapor-liquid systems; when the density of the fluid is high, the only instability which occurs is that the liquid must flash to produce vapor as the temperature is raised.

In Figure 7 is shown the stability limit in a hydrogen sulfide-methane mixture which is capable of liquid-liquid separations. Here, as volume decreases the stability limit extends to high positive pressures. The region of instability is always to the right

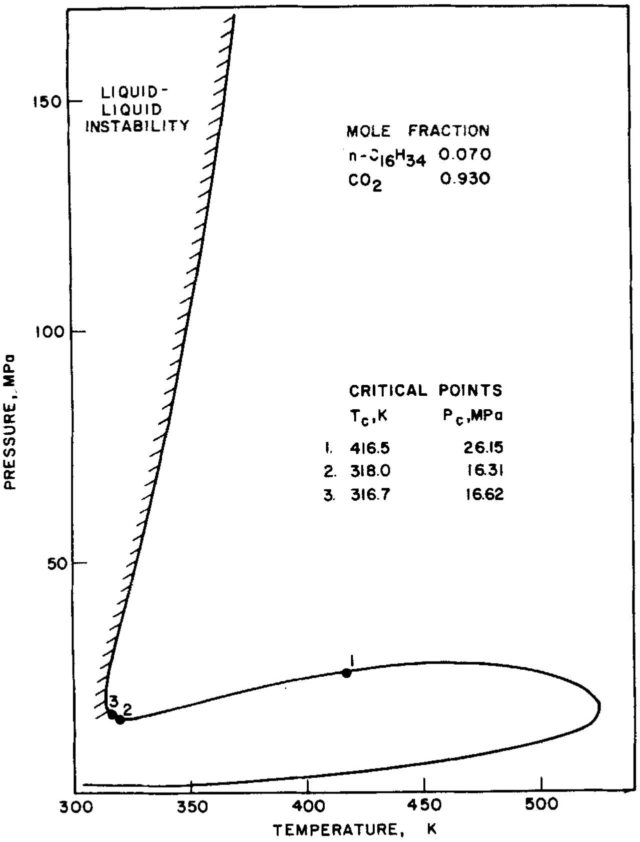

Figure 10. Stability limit for a mixture with three calculated critical points.

of the stability limit curve when moving in the direction of increasing volume. The figure indicates that the high density fluid must separate into two (or more) phases as the temperature decreases.

Low temperature equilibrium data in the hydrogen sulfide-methane system are given by Kohn and Kurata (1958). These

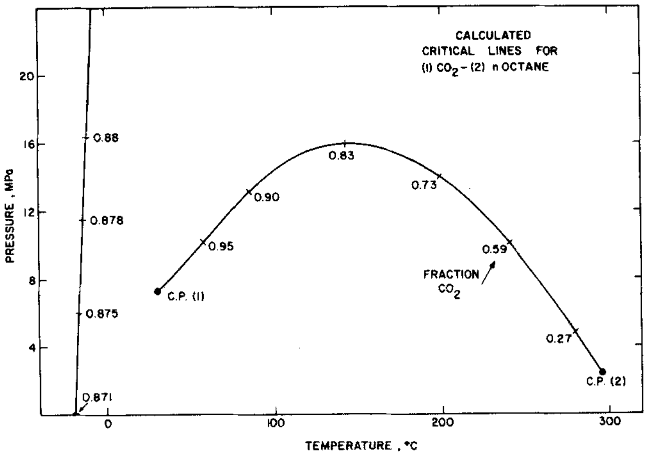

Figure 11. Calculated critical lines for $CO_2-nC_8H_{18}$, showing separate liquid-liquid critical points.

data show that liquid-liquid separations occur when the hydrogen sulfide fraction is between about 6.5 and 90 mole %. Figure 7, for 77.1% hydrogen sulfide, correctly indicates that liquid-liquid separations occur.

Another possible shape of the stability limit curve is shown in Figure 8. For a mixture with 49% hydrogen sulfide in methane, the curve extends directly to high pressures without first entering the negative pressure region.

In Figures 7 and 8 a fair picture can be obtained of the coexistence region boundary from the stability limit curves. The two curves are tangent at the critical point, and the region of instability lies inside the two-phase region.

High Density Critical Points

Figure 9 shows the cubic form (the second critical point criterion) plotted against volume for 49% hydrogen sulfide and 51% methane. As in Figure 3 (which is drawn for a seven-

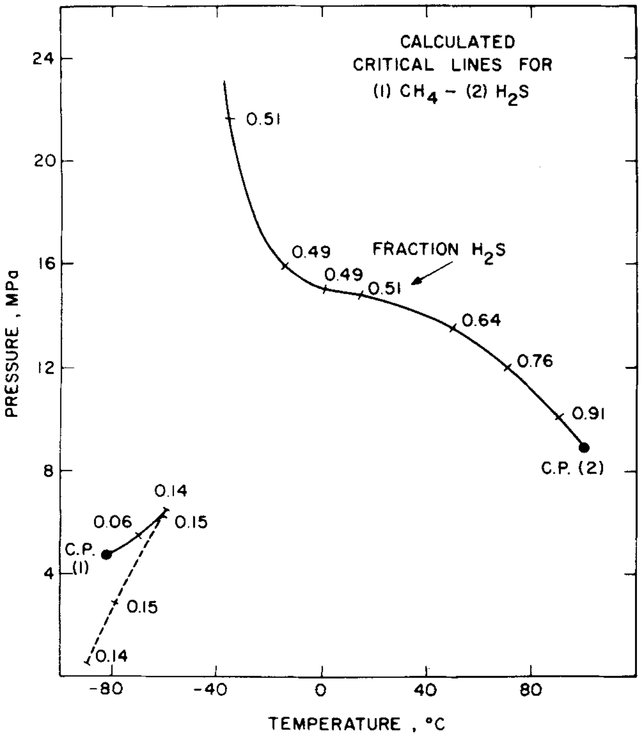

Figure 12. Critical lines for CH_4-H_2S. Liquid-liquid and vapor-liquid branches interact.

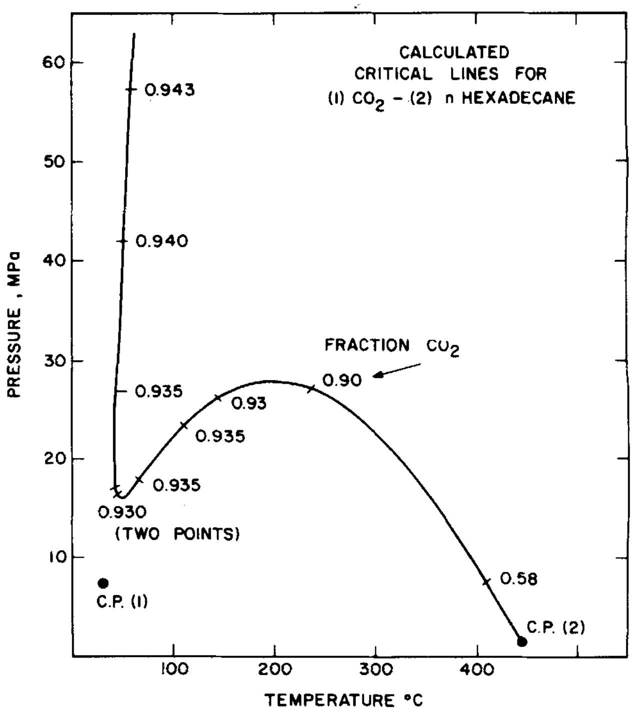

Figure 13. Critical lines for $CO_2-nC_{16}H_{34}$, showing mixtures with three critical points.

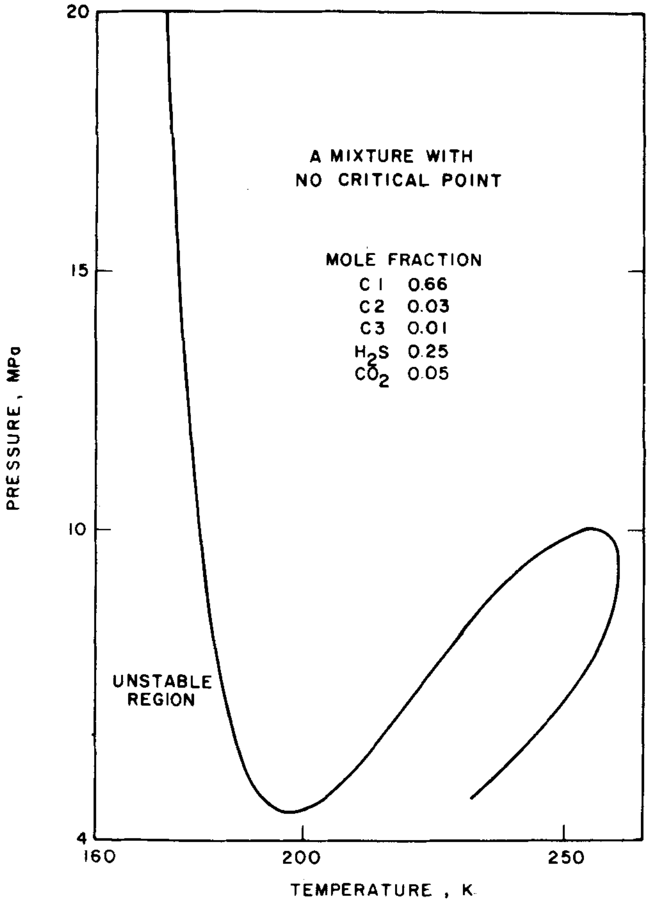

Figure 14. Stability limit for a mixture with no critical point, showing vapor-liquid and liquid-liquid separations.

component system), the cubic form is zero at more than one point along the stability limit, and it becomes necessary to determine whether the higher density point can be taken to be a critical point.

As shown in Figure 8, both potential critical points fall at positive pressures, and there is no obvious reason to discount that both are critical points.

In Figure 10, drawn for a mixture of 93.0% carbon dioxide in *n*-hexadecane, there is a still more complex picture with three critical points indicated by the critical point criteria.

These additional critical points were found by constructing the cubic form, as in Figure 9, and choosing as the initial guess a volume near the desired root. The initial guess $v = 4b$ converges to a root at a volume greater than the point of the first maximum in the cubic form.

It should be noted that Scott and van Konynenburg (1970, 1972) were concerned with locating all possible critical points in their study of binary mixtures. The calculation procedure they used rested on eliminating temperature between the two critical criteria and searching for sign changes in the resulting function of volume only. The calculation procedure we have used has a similar character.

In systems like carbon dioxide-*n* octane, the high density critical points have a clear-cut physical significance; such points are upper critical solubility temperatures in the liquid phase. The calculated critical lines for this binary system are shown in Figure 11, where mixtures containing about 82% carbon dioxide are shown to have both vapor-liquid and liquid-liquid critical points.

In other systems, however, the distinction between vapor-liquid and liquid-liquid behavior becomes very difficult. Schneider (1968) has argued that "many phenomena could only be understood if continuous transitions between these two forms of phase equilibria occurred."

We are not aware of any measurements which would indicate that two or three critical points can be found on a continuous coexistence curve, as seems to be required by Figures 9 and 10, although the calculations of Scott and van Konynenburg (1970, 1972) do contain examples similar to these. The data for hydrogen sulfide-methane (Kohn and Kurata, 1958) and for carbon dioxide-*n*-hexadecane (Schneider et al, 1967) do not indicate that the experimenters were aware of such phenomena. Neither do the extensive reviews of critical behavior by Hicks and Young (1975) or Schneider (1978) contain mention of the possibility. However, the behavior is plausible, if considered in the light suggested by Schneider that the transition between liquid-liquid and liquid-vapor behavior is continuous.

Calculated critical lines for methane-hydrogen sulfide and carbon dioxide-*n*-hexadecane are shown in Figures 12 and 13, with the mole fraction of one of the components as a parameter. The critical lines are discontinuous. In both binary systems, the critical line beginning at the lower temperature critical point should terminate at a three-phase L_1-L_2-G line which we have not calculated. Extending beyond this line, the critical line displays a cusp and more than one critical point for some compositions. In this region, some of the calculated critical points will apply to metastable or unstable phases which could not be observed experimentally because of the liquid-liquid separations. (Details are not shown in Figure 13 because the region involved is very small compared to the scale of the figure.)

Systems With No Critical Points

As pointed out by Peng and Robinson (1977), some systems have no critical point. This is true of some methane-hydrogen sulfide and carbon dioxide-hydrocarbon mixtures. A stability limit curve for a mixture with no critical point is shown in Figure 14.

For such systems, the maximum of the cubic form lies below $C = 0$. It appears that the transition from a system with two critical points (49% hydrogen sulfide in methane) to a system with no critical point (48% hydrogen sulfide in methane) takes place at the composition where the maximum point of the cubic form becomes just tangent to the line $C = 0$. On the stability limit curve, the two critical points would move closer together, then converge and vanish as this point was reached.

Whether this sort of transition occurs in the experiments we do not know. Kohn and Kurata (1958) assume that it is interference with a three-phase L_1-L_2-S line that prevents some methane-hydrogen sulfide mixtures from showing a critical point. Calculations like ours, with equations of state, indicate other possibilities.

DISCUSSION

The formulation presented for the critical point criteria was used in the development of a computational procedure for critical points in vapor-liquid equilibria. Some examples show how the procedure can be modified to permit computation of all possible critical points in a given mixture or to determine whether a given mixture has a critical point.

The calculation procedure is robust and converged, in all the systems so far studied, in three to five iterations. It has been possible to apply the procedure to critical point calculations in systems containing up to forty-three components.

The stability limit projection on the P-T plane proved to be a significant aid in understanding the rather complex behavior possible in mixtures with high density phase separations.

ACKNOWLEDGMENT

This work was supported by the National Research Council of Canada.

APPENDIX

The SRK equation is

$$P = RT/(v - b) - a/[v(v + b)] \tag{A1}$$

where a and b in a mixture are found from

$$b = \sum_j \sum_i y_i y_j b_{ij} \tag{A2}$$

$$a = \sum_j \sum_i y_i y_j a_{ij} \tag{A3}$$

For pure components

$$a_{ii} = \alpha_i(T)\,(0.42748\, R^2 T_{c_i}^{\,2}/P_{c_i}) \tag{A4}$$

where

$$\alpha_i(T) = [1 + m_i\,(1 - \sqrt{T/T_{c_i}})]^2 \tag{A5}$$

$$m_i = 0.480 + 1.574\,\omega_i - 0.176\,\omega_i^{\,2} \tag{A6}$$

and

$$b_{ii} = 0.08664\; RT_{c_i}/P_{c_i} \tag{A7}$$

Our derivation is suitable for a model with two interaction parameters:

$$a_{ij} = (1 - k_{ij})\sqrt{a_{ii}a_{jj}} \tag{A8}$$

and

$$b_{ij} = (1 - c_{ij})(b_{ii} + b_{jj})/2 \tag{A9}$$

With these mixing rules

$$\ln(f_i) = \ln[y_i RT/(v - b)] + \beta_i/(v - b) + \frac{a\beta_i}{RTb^2}\left[\ln\left(\frac{v+b}{v}\right) - \frac{b}{(v+b)}\right] - \frac{\alpha_i}{RTb}\ln\left(\frac{v+b}{v}\right) \tag{A10}$$

where

$$\alpha_i = 2\sum_j y_j a_{ij} \tag{A11}$$

and

$$\beta_i = 2\sum_j y_j b_{ij} - b \tag{A12}$$

The derivatives in the quadratic form are

$$n_T\left(\frac{\partial \ln f_i}{\partial n_j}\right) = \frac{\delta_{ij}}{y_i} + \frac{2b_{ij}}{v - b} + \frac{\beta_i\beta_j}{(v-b)^2} + \frac{a\beta_i\beta_j}{RTb}\cdot\frac{1}{(v+b)^2} + \frac{B_1}{RTb^2}\cdot\frac{1}{(v+b)} + \frac{B_2}{RTb^3}\ln\left(\frac{v+b}{v}\right) \tag{A13}$$

where

$$\delta_{ij} = \begin{cases} 0, & i \neq j \\ 1, & i = j \end{cases} \tag{A14}$$

$$\gamma_{ij} = 2b_{ij} - \beta_i - \beta_j \tag{A15}$$

$$B_1 = 2a\beta_i\beta_j - b(\alpha_i\beta_j + \alpha_j\beta_i + a\gamma_{ij}) \tag{A16}$$

and

$$B_2 = -B_1 - 2a_{ij}b^2 \tag{A17}$$

The terms in the cubic form are

$$n_T^{\,2}\left(\frac{\partial^2 \ln f_i}{\partial n_k \partial n_j}\right) = -\frac{\delta_{ijk}}{y_i^{\,2}} + \frac{2C_1 - C_2}{(v-b)^2} + \frac{2C_3}{(v-b)^3} - \frac{2aC_3}{RTb}\cdot\frac{1}{(v+b)^3} + \frac{D}{RTb^2}\cdot\frac{1}{(v+b)^2} + \frac{E}{RTb^3}\cdot\frac{1}{(v+b)} - \frac{E}{RTb^4}\ln\left(\frac{v+b}{v}\right) \tag{A18}$$

where

$$\delta_{ijk} = \begin{cases} 1, & i = j = k \\ 0, & i \neq j,\ j \neq k, \text{ or } i \neq k \end{cases} \tag{A19}$$

and where

$$C_1 = b_{ij}\beta_k + b_{ij}\beta_j + b_{jk}\beta_i \tag{A20}$$

$$C_2 = \beta_i\beta_j + \beta_i\beta_k + \beta_j\beta_k \tag{A21}$$

$$C_3 = \beta_i\beta_j\beta_k \tag{A22}$$

$$C_4 = \gamma_{ij} + \gamma_{ik} + \gamma_{jk} \tag{A23}$$

$$C_5 = \gamma_{ij}\beta_k + \gamma_{ik}\beta_j + \gamma_{jk}\beta_i \tag{A24}$$

$$C_6 = a_{ij}\beta_k + a_{ik}\beta_j + a_{jk}\beta_i \tag{A25}$$

$$C_7 = \alpha_i\gamma_{jk} + \alpha_j\gamma_{ik} + \alpha_k\gamma_{ij} \tag{A26}$$

$$C_8 = \alpha_i\beta_j\beta_k + \alpha_j\beta_i\beta_k + \alpha_k\beta_i\beta_j \tag{A27}$$

$$D = b(aC_5 + C_8) - 3C_3 \cdot a \tag{A28}$$

$$E = 2D - b^2(2C_6 + C_7 - aC_4) \tag{A29}$$

NOTATION

A = Helmholtz free energy
a, b = parameters in the equation of state
C = cubic form
f_i = fugacity of component i
h_{ijk} = integer, Equation (31)
i = number of iterations
k = constant
N = number of components
n_i = moles of component i
P = pressure
$\mathbf{Q}$ = matrix in the quadratic form
Q = determinant of $\mathbf{Q}$
q_{ij} = element of $\mathbf{Q}$
R = gas constant
S = entropy
S_0 = entropy in unvaried state
T = absolute temperature
t = time
T_{c_i} = pure component critical temperature
V = volume
v = molar volume
y_i = mole fraction
μ = chemical potential
ω = Pitzer's acentricity

Subscripts

c = critical property
i,j,k = component numbers

LITERATURE CITED

Baker, L. E. and K. D. Luks, "Critical Point and Saturation Pressure Calculations for Multicomponent Systems," paper number SPE-7478 presented at the Houston Meeting of the Petroleum Society of the AIME (1978).

Beegle, B. L., M. Modell and R. C. Reid, "Legendre Transforms and their Applications to Thermodynamics," *AIChE J.*, **20**, 1194 (1974*a*).

———, "Thermodynamic Stability Criterion for Pure Substances and Mixtures," *ibid.*, 1200 (1974*b*).

Burden, R. L., J. D. Faires and A. C. Reynolds, *Numerical Analysis*, Prindle, Weber and Schmidt, Boston, Mass. (1978).

Deiters, U. and G. M. Schneider, "Fluid Mixtures at High Pressures. Computer Calculations of the Phase Equilibria and the Critical Phenomena in Fluid Binary Mixtures from the Redlich-Kwong Equation of State," *Ber. der Bunsenges. physik Chem.*, **80**, 1316 (1976).

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

Hicks, C. P. and C. L. Young, "The Gas-Liquid Critical Properties of Binary Mixtures," *Chem. Rev.*, **75**, 119 (1975).

Kohn, J. P. and F. Kurata, "Heterogeneous Phase Equilibria of the Methane-Hydrogen Sulfide System," *AIChE J.*, 4, 211 (1958).

Modell, M., and R. C. Reid, *Thermodynamics and its Applications*, Prentice-Hall, Inc., Englewood Cliffs, N.J. (1974).

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

———, "A Rigorous Method for Predicting the Critical Properties of Multicomponent Systems from an Equation of State," *AIChE J.*, **23**, 137 (1977).

Reid, R. C., and B. L. Beegle, "Critical Point Criteria in Legendre Transform Notation," *ibid.*, 726 (1977).

Schneider, G., "Phase Equilibria in Binary Fluid Systems of Hydrocarbons with Carbon Dioxide, Water, and Methane," *Chem. Eng. Progr. Symposium Ser. No. 88*, **64**, 9 (1968).

———, "High-pressure Phase Diagrams and Critical Properties of Fluid Mixtures," *Chemical Thermodynamics, A Specialist Periodical Report*, Vol. 2, Chapt. 4, The Chemical Society, London, England (1978).

Schneider, G., Z. Alwani, E. Horvath and E. U. Franck, "Phasengleichgewichte und kritische Erscheinungen in binären Mischsystemen bis 1500 bar," *Chemie-Ing. - Techn.*, 39, 649 (1967).

Scott, R. L. and P. H. van Konynenburg, "Static Properties of Solutions. Van der Waals and Related Models for Hydrocarbon Mixtures," *Disc. Faraday Soc.*, 49, 87 (1970).

Scott, R. L., "The Thermodynamics of Critical Phenomena in Fluid Mixtures," *Ber. Bunsenges. physik Chem.* **76**, 296 (1972).

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

Spear, R. R., R. L. Robinson, Jr., and K. C. Chao, "Critical State of Ternary Mixtures and Equations of State," *Ind. Eng. Chem. Fundamentals*, **10**, 591 (1971).

Spencer, C. F., T. E. Daubert and P. D. Danner, "A Critical Review of Correlations for the Critical Properties of Defined Mixtures," *AIChE J.*, **19**, 522 (1973).

Teja, A. S. and H. W. Kropholler, "Critical States of Mixtures in Which Azeotropic Behavior Persists in the Critical Region," *Chem. Eng. Sci.*, **30**, 435 (1975).

Teja, A. S. and J. S. Rowlinson, "The Prediction of Thermodynamic Properties of Fluids and Fluid Mixtures - IV. Critical and Azeotropic States," *ibid.*, **28**, 529 (1973).

Wilson, G. M., "A Modified Redlich-Kwong Equation of State, Application to General Physical Data Calculations," paper presented at the 65th National AIChE Meeting, Cleveland, Ohio (1969).

Yu, R. K. F., "An Investigation of Vaporization in the Displacement of Swan Hills Crude Oil by Rich Gas," M. Eng. thesis, Univ. Calgary, Canada (1975).

Manuscript received April 2, 1979; revision received March 3, and accepted March 13, 1980.

The Extended Graetz Problem with Prescribed Wall Flux

ELEFTHERIOS PAPOUTSAKIS
DORAISWAMI RAMKRISHNA
and
HENRY C. LIM
School of Chemical Engineering
Purdue University
West Lafayette, Indiana 47907

An analytical solution is obtained to the extended Graetz problem with prescribed wall flux, based on a selfadjoint formalism resulting from a decomposition of the convective diffusion equation into a pair of first-order partial differential equations. The solution obtained is simple, computationally efficient and in striking contrast with incomplete numerical efforts in the past.

SCOPE

The joint effects of convective and molecular transport play an important role in all contacting operations, the purpose of which is the selective movement of mass and/or energy from one phase to another. The analysis of such transport depends on the solution of the so-called convective, diffusion, differential equations subject to suitable boundary conditions. Specifically, the transport of mass or energy in fully developed laminar flow through a circular tube (or between parallel plates) has been of traditional interest. This problem, without accounting for axial molecular transport, has been called the Graetz problem. The extension of the Graetz problem to include axial conduction or diffusion, which becomes necessary for small values of an axial Peclet number, is important, for example, in dealing with heat transfer in liquid metals. Papoutsakis, Ramkrishna and Lim (1980) have reviewed past efforts in dealing with the foregoing extended Graetz problem and have provided an analytical solution to the case where the tube-wall temperature is specified. This solution, which is in sharp contrast with the approximate methods employed previously, depends on the use of a selfadjoint formalism employed by Ramkrishna and Amundson (1979) to solve certain apparently nonselfadjoint problems in heat conduction.

The present paper is an extension of the work of Papoutsakis et al. (1980) to include the case of the Neumann boundary condition for the extended Graetz problem, that is, where the energy flux at the tube wall has been specified.

CONCLUSIONS AND SIGNIFICANCE

The present work produces an analytical solution to the extended Graetz problem with finite and infinite energy or mass exchange sections and prescribed wall energy or mass fluxes, with an arbitrary number of discontinuities. The solution obtained is as simple in form and efficient computationally as the solution of the corresponding classical Graetz problem. Extensions of the solution methodology to problems with more general boundary conditions can be made in a straightforward manner.

The effect of the finite heating section length, although most important in the low Peclet number range, is significant even at Peclet numbers higher than 30, particularly close to the wall

---

Correspondence concerning this paper should be addressed to Doraiswami Ramkrishna. Eleftherios Papoutsakis is with the Department of Chemical Engineering, Rice University, Houston, Texas 77001.

0001-1541-80-3297-0779-$01.05.