

CALCULATION OF CRITICAL POINTS AND PHASE BOUNDARIES IN THE CRITICAL REGION

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ABSTRACT

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A computationally efficient, general method is presented for calculating the critical temperature and pressure of a multicomponent mixture of specified composition. The procedure suggested also provides coefficients α_T , α_P and u relating changes in temperature, pressure, phase fraction β and composition in the immediate vicinity of the critical point. These variations are shown to be of the general form

$$T - T_c = \alpha_T (1 - 2\beta) \delta$$

$$P - P_c = \alpha_P (1 - 2\beta) \delta$$

$$\ln K_i = u_i z_i^{-1/2} \delta$$

where δ is the distance parameter of the phase-boundary expansion. Finally, an explicit first-order approximation is developed, based on derivatives of the Gibbs-energy surface, giving the phase fractions and equilibrium phase composition for a mixture under near-critical conditions.

INTRODUCTION

A generally applicable procedure for the calculation of critical points for multicomponent mixtures described by a single equation of state has recently been developed by Heidemann and Khalil (1980). This procedure, which requires no user-provided initial estimates of the critical temperature and pressure, uses nested iterations, where the temperature corresponding to the limit of intrinsic stability at a specified molar volume is determined in an inner loop, while the molar volume is varied in the outer loop to satisfy the condition that a cubic form evaluated at the stability limit must equal zero.

The method to be described here is based on the criticality criteria given by Michelsen (1982b). The critical temperature and pressure are determined

by direct Newton–Raphson iteration, and a definite deficiency of the method is that, using T and P as the independent variables, rather close initial estimates are required. However, the method has the advantage of being very cost-efficient with respect to evaluations of thermodynamic properties and the associated algebraic operations. In addition, the partial derivatives required by the algorithm are those normally applied in phase equilibrium calculations.

A more important aspect of the method is that the quantities calculated for critical-point determination can be related to relative changes in temperature, pressure and the composition and distribution of the equilibrium phases in the critical region.

CRITICALITY CONDITIONS

Let the N -component mixture for which the critical temperature T_c and critical pressure P_c are desired be of composition \mathbf{z} . The criticality conditions used here are based on tangent-plane stability criterion of Gibbs as modified by Michelsen (1982a). The necessary and sufficient criterion for stability at a specified temperature and pressure (T, P) is that

$$F(\mathbf{Y}) = 1 + \sum_i Y_i [\ln Y_i + \ln \phi_i(\mathbf{Y}) - \ln z_i - \ln \phi_i(\mathbf{z}) - 1] \geq 0 \quad (1)$$

for any trial phase mole numbers \mathbf{Y} . We shall use the term “locally stable” for a mixture provided that there exists a closed region $\|\mathbf{Y} - \mathbf{z}\| < \epsilon$, within which F is nonnegative everywhere. At a critical point a specific behaviour of F , to be described below, is required.

The first and second partial derivatives of F with respect to the Y_i are

$$\partial F / \partial Y_i = g_i = \ln Y_i + \ln \phi_i(\mathbf{Y}) - \ln z_i - \ln \phi_i(\mathbf{z}) \quad (2)$$

and

$$\partial^2 F / \partial Y_i \partial Y_j = (1/Y_i) \delta_{ij} + (\partial \ln \phi_i / \partial n_j)_{\mathbf{Y}} \quad (3)$$

It is convenient to substitute as new independent variables a set of deviation variables \mathbf{X} given by

$$X_i = (Y_i - z_i) / v_i \quad (4)$$

with $v_i = z_i^{1/2}$. In terms of these variables, the above partial derivatives become

$$\partial F / \partial X_i = v_i g_i$$

and

$$\partial^2 F / \partial X_i \partial X_j = v_i v_j (\partial^2 F / \partial Y_i \partial Y_j) \quad (5)$$

In particular,

$$\left(\partial^2 F / \partial X_i \partial X_j\right)_{\mathbf{x}=\mathbf{0}} = B_{ij} = \delta_{ij} + v_i v_j (\partial \ln \phi_i / \partial n_j)_z \quad (6)$$

The transformation leads to a scaling of the matrix of second derivatives such that this matrix becomes the identity matrix for an ideal mixture.

We introduce a distance parameter s and select $\mathbf{X} = s\mathbf{u}$, where \mathbf{u} is a vector of unit length, $\mathbf{u}^T \mathbf{u} = 1$. Considering F in dependence on s along this line, the following Taylor-series expansion is obtained:

$$\begin{aligned} F(\mathbf{X} = s\mathbf{u}) &= F_1(s) = \sum_{m=0}^{\infty} (s^m/m!)(d^m F_1/ds^m)_{s=0} \\ &= as + bs^2 + cs^3 + ds^4 + O(s^5) \end{aligned} \quad (7)$$

since $F_1(0) = 0$. In addition, $a = \sum_i n_i g_i(s=0) = 0$, and for sufficiently small values of s the series is dominated by the s^2 term. A necessary condition for stability is therefore that

$$b = (1/2) \sum_{i,j} B_{ij} u_i u_j = (1/2) \mathbf{u}^T \mathbf{B} \mathbf{u} \geq 0 \quad (8)$$

regardless of the choice of \mathbf{u} . The smallest value of the quadratic form (eqn. (8)) is attained by choosing \mathbf{u} as the eigenvector of \mathbf{B} corresponding to the smallest eigenvalue λ_{\min} , or

$$\mathbf{B}\mathbf{u} = \lambda_{\min} \mathbf{u}, \mathbf{u}^T \mathbf{u} = 1 \quad (9)$$

yielding $b = \lambda_{\min}/2$. If this value of b is positive, the system is locally stable. If b is negative, the system is intrinsically unstable, and if b equals zero, the system is at the limit of intrinsic stability. The first condition that must hold at a critical point is that b equals zero, i.e., $\lambda_{\min} = 0$. The second condition that must hold is that the value of c corresponding to the eigenvector \mathbf{u} is also zero. A nonzero value of c with $b=0$ implies that the mixture is intrinsically unstable, since F_1 becomes negative for sufficiently small positive (if c is negative) or negative (if c is positive) values of s . Hence a critical point is a point where, selecting \mathbf{u} as the eigenvector of \mathbf{B} corresponding to λ_{\min} , both b and c in eqn. (7) equal zero. Local stability at the critical point requires at least that $d \geq 0$.

The numerical evaluation of b , c and d is performed conveniently as follows. At the trial conditions (T, P) , \mathbf{B} is calculated and $(\lambda_{\min}, \mathbf{u})$ are determined by inverse iteration (Wilkinson, 1965, Chap. 9). This yields the coefficient b . For c , Michelsen (1982b) suggested the following numerical determination. The derivative

$$dF_1/ds = 2bs + 3cs^2 + 4ds^3 + O(s^4) \quad (10)$$

equals

$$\sum_i (\partial F / \partial Y_i) dY_i / ds = \sum_i v_i u_i g_i \quad (11)$$

Since b is known, a single calculation of F and the g_i (eqn. (2)) at a small value of s , $s = \epsilon$, allows c (and d) to be determined. In particular, note that

$$4F_1(\epsilon) - \epsilon(dF_1/ds)_\epsilon = 2b\epsilon^2 + c\epsilon^3 + O(\epsilon^5) \quad (12)$$

from which

$$c = (1/\epsilon^3)[4F_1(\epsilon) - \epsilon(dF_1/ds)_\epsilon - 2b\epsilon^2] + O(\epsilon^2) \quad (13)$$

Similarly,

$$d = (1/\epsilon^4)[3F_1(\epsilon) - \epsilon(fF_1/ds)_\epsilon - b\epsilon^2] + O(\epsilon) \quad (14)$$

Alternatively, the method of central differences, that is, evaluation of dF_1/ds at $s = \epsilon$ and $s = -\epsilon$, yields

$$c = (1/6\epsilon^2)[(dF_1/ds)_\epsilon + (dF_1/ds)_{-\epsilon}] + O(\epsilon^2) \quad (15)$$

and

$$d = (1/8\epsilon^3)[(dF_1/ds)_\epsilon - (dF_1/ds)_{-\epsilon} - 4b\epsilon] + O(\epsilon^2) \quad (16)$$

that is, both c and d are obtained with an error proportional to ϵ^2 .

ITERATIVE DETERMINATION OF CRITICAL POINT

The objective is to locate the temperature and pressure at which b and c are both equal to zero. New trial values are generated by Newton–Raphson iteration, solving the equations

$$\begin{pmatrix} b_T & b_P \\ c_T & c_P \end{pmatrix}_m \begin{pmatrix} \Delta T \\ \Delta P \end{pmatrix} = \begin{pmatrix} -b \\ -c \end{pmatrix}_m \quad (17)$$

and

$$\begin{pmatrix} T \\ P \end{pmatrix}_{m+1} = \begin{pmatrix} T \\ P \end{pmatrix}_m + \begin{pmatrix} \Delta T \\ \Delta P \end{pmatrix} \quad (18)$$

where b and c represent the coefficients at the m th iteration and the subscripts T and P denote their partial derivatives with respect to temperature and pressure. These partial derivatives can, of course, be determined by numerical differentiation, but a much more inexpensive evaluation is possible.

Differentiation of eqn. (9) with respect to pressure yields

$$\mathbf{B}u_P + \mathbf{B}_P u = \lambda_{\min} u_P + \lambda_P u \quad (19)$$

and

$$\mathbf{u}^T \mathbf{u}_p = 0 \quad (20)$$

where λ_p and \mathbf{u}_p are respectively the pressure derivative of λ_{\min} and the corresponding eigenvector, and \mathbf{B}_p is the pressure derivative of the matrix \mathbf{B} . Multiplication of eqn. (19) by \mathbf{u}^T yields λ_p directly:

$$\mathbf{u}^T \mathbf{B} \mathbf{u}_p + \mathbf{u}^T \mathbf{B}_p \mathbf{u} = \lambda_{\min} \mathbf{u}^T \mathbf{u}_p + \lambda_p \mathbf{u}^T \mathbf{u} \quad (21)$$

or

$$\lambda_p = \mathbf{u}^T \mathbf{B}_p \mathbf{u} \quad (22)$$

since $\mathbf{u}^T \mathbf{B} = \lambda_{\min} \mathbf{u}^T$ and $\mathbf{u}^T \mathbf{u}_p = 0$. Equation (19) can now be solved for \mathbf{u}_p :

$$(\mathbf{B} - \lambda_{\min} \mathbf{I}) \mathbf{u}_p = \mathbf{v} \quad (23)$$

with $\mathbf{v} = \lambda_p \mathbf{u} - \mathbf{B}_p \mathbf{u}$. The matrix of coefficients for this set of N linear equations is of rank $N - 1$, and the augmented matrix $(\mathbf{B} - \lambda_{\min} \mathbf{I}, \mathbf{v})$ is also of rank $N - 1$. Hence the general solution of eqn. (23) is

$$\mathbf{u}_p = \mathbf{h} + Q \mathbf{u} \quad (24)$$

where \mathbf{h} is any particular solution to eqn. (23) and Q is an arbitrary scalar multiplier. Solving for \mathbf{h} , Q is determined from the condition given as eqn. (20), yielding $Q = -\mathbf{u}^T \mathbf{h}$. The numerical procedure for solving the set of homogeneous linear equations is described in Appendix A.

Explicit numerical evaluation of \mathbf{B}_p is not required, since only the vector $\mathbf{B}_p \mathbf{u}$ is needed. The elements of this vector can be found from

$$\begin{aligned} (\mathbf{B}_p \mathbf{u})_i &= v_i \sum_j v_j u_j \left(\partial^2 \ln \phi_i / \partial n_j \partial P \right)_z = v_i \frac{\partial}{\partial s} \left(\partial \ln \phi_i(\mathbf{Y}) / \partial P \right)_{s=0} \\ &= v_i (1/\epsilon) \left[\left(\partial \ln \phi_i / \partial P \right)_{s=\epsilon} - \left(\partial \ln \phi_i / \partial P \right)_{s=0} \right] + O(\epsilon) \end{aligned} \quad (25)$$

or, alternatively, by taking central differences between the pressure derivatives at $s = \epsilon$ and $s = -\epsilon$. The derivative b_p equals $\lambda_p/2$. The derivative of c with respect to P is found using eqn. (7):

$$\partial F_1 / \partial P = s^2 b_p + s^3 c_p + s^4 d_p + \dots \quad (26)$$

Pressure differentiation using eqn. (1) yields

$$\partial F_1 / \partial P = \sum_i Y_i \left[\left(\partial \ln \phi_i / \partial P \right)_v - \left(\partial \ln \phi_i / \partial P \right)_z \right] + \sum_i g_i \left(\partial Y_i / \partial P \right) \quad (27)$$

where $\partial Y_i / \partial P = (\partial Y_i / \partial u_i) \partial u_i / \partial P = s v_i (\mathbf{u}_p)_i$. Evaluation of eqn. (27) at $s = \epsilon$ then yields

$$c_p = (1/\epsilon^3) \left[\left(\partial F_1 / \partial P \right)_{s=\epsilon} - b_p \epsilon^2 \right] + O(\epsilon) \quad (28)$$

or, using an additional evaluation at $s = -\epsilon$,

$$c_P = (1/2\epsilon^3) [(\partial F/\partial P)_{s=\epsilon} - (\partial F/\partial P)_{s=-\epsilon}] + O(\epsilon^2) \quad (29)$$

The temperature derivatives of b and c are found similarly.

In conclusion, note that all of the quantities needed for a single Newton–Raphson iteration can be evaluated from a calculation of the partial derivatives of the fugacity coefficients with respect to composition, temperature and pressure at the mixture composition \mathbf{z} , supplemented by one (or, if desired, two) additional calculations of the fugacity coefficients and their partial derivatives with respect to temperature and pressure at a perturbed composition. The additional calculation using central differences may well be advisable, since very small values of ϵ will result in excessive round-off errors (e.g., in the division by ϵ^3). On the other hand, only approximate values of the pressure and temperature derivatives of b and c are needed. The parameter b is found exactly, and c can be found from eqn. (9) with an error of ϵ^2 , using only a single fugacity-coefficient calculation. In the author's opinion, central differences do provide more safety, and $\epsilon = 10^{-3}$ (on a 16-digit machine) is a reasonable choice.

The algebraic overhead is very modest. The inverse iteration for λ_{\min} and \mathbf{u} requires a single triangular decomposition of \mathbf{B} , and the triangular factors can be utilized for the solution of eqn. (23).

LOCAL STABILITY OF THE CRITICAL POINT

A Taylor-series expansion of F in the deviation variables \mathbf{X} including terms up to fourth order gives

$$\begin{aligned} F(\mathbf{X}) = F(\mathbf{0}) + \sum_i A_i X_i + (1/2) \sum_{i,j} B_{ij} X_i X_j + (1/6) \sum_{i,j,k} C_{ijk} X_i X_j X_k \\ + (1/24) \sum_{i,j,k,l} D_{ijkl} X_i X_j X_k X_l + \dots \end{aligned} \quad (30)$$

where $A_i = (\partial F/\partial X_i)_{\mathbf{X}=\mathbf{0}} = 0$, $B_{ij} = (\partial^2 F/\partial X_i \partial X_j)_{\mathbf{X}=\mathbf{0}}$ (our previous \mathbf{B}), etc. \mathbf{X} may be expanded as

$$\mathbf{X} = s\mathbf{u} + s^2\mathbf{w} + s^3\mathbf{q} + \dots \quad (31)$$

with $\mathbf{u}^T \mathbf{u} = 1$, and where \mathbf{w} and \mathbf{q} are yet undetermined vectors which are orthogonal to \mathbf{u} , i.e.,

$$\mathbf{u}^T \mathbf{w} = \mathbf{u}^T \mathbf{q} = 0 \quad (32)$$

Substituting eqn. (31) in the expansion and combining equal powers of s yields

$$\begin{aligned}
 F = s^2 & \left[(1/2) \sum_{i,j} B_{ij} u_i u_j \right] + s^3 \left[\sum_{i,j} B_{ij} w_i u_j + (1/6) \sum_{i,j,k} C_{ijk} u_i u_j u_k \right] \\
 & + s^4 \left[\sum_{i,j} B_{ij} (q_i u_j + w_i w_j / 2) + (1/2) \sum_{i,j,k} C_{ijk} w_i u_j u_k \right. \\
 & \left. + (1/24) \sum_{i,j,k,l} D_{ijkl} u_i u_j u_k u_l \right] \quad (33)
 \end{aligned}$$

Selecting \mathbf{u} to minimize the coefficient of s^2 yields the previous result, $\mathbf{B}\mathbf{u} = \lambda_{\min} \mathbf{u}$. Furthermore, the (i, j) cross-products are zero, i.e.,

$$\sum_{i,j} B_{ij} w_i u_j = \sum_{i,j} B_{ij} q_i u_j = 0 \quad (34)$$

since $\sum_j B_{ij} u_j = \lambda_{\min} u_i$, and \mathbf{u} is orthogonal to \mathbf{w} and \mathbf{q} . The terms in eqn. (33) which contain only elements of \mathbf{u} are identical to the coefficients b , c and d defined earlier. Finally, let $r_i = (1/2) \sum_{jk} C_{ijk} u_j u_k$. Then

$$F = bs^2 + cs^3 + s^4 \left[(1/2) \sum_{i,j} B_{ij} w_i w_j + \sum_i r_i w_i + d \right] \quad (35)$$

\mathbf{w} is selected to minimize the coefficient of s^4 , subject to the constraint $\mathbf{u}^T \mathbf{w} = 0$. This coefficient is quadratic in \mathbf{w} , and provided that \mathbf{B} has at most a single nonpositive eigenvalue (λ_{\min}), there exists a unique minimizer given (Fletcher, 1981, Chap. 10) by

$$\mathbf{B}\mathbf{w}^* + [\mathbf{r} - (\mathbf{u}^T \mathbf{r}) \mathbf{u}] = \mathbf{0}, \quad \mathbf{u}^T \mathbf{w}^* = 0 \quad (36)$$

The elements of \mathbf{r} can be evaluated from quantities already calculated. From eqn. (30) where $A_i = 0$,

$$\partial F / \partial X_i = \sum_j B_{ij} X_j + (1/2) \sum_{j,k} C_{ijk} X_j X_k + \dots \quad (37)$$

or, using $\mathbf{X} = \epsilon \mathbf{u}$,

$$(\partial F / \partial X_i)_\epsilon = \epsilon \lambda_{\min} u_i + \epsilon^2 r_i + O(\epsilon^3) \quad (38)$$

that is,

$$r_i = (1/\epsilon^2) [v_i g_i(s = \epsilon) - \epsilon \lambda_{\min} u_i] + O(\epsilon) \quad (39)$$

or

$$r_i = (1/2\epsilon^2) v_i [g_i(s = \epsilon) - g_i(s = -\epsilon)] + O(\epsilon^2) \quad (40)$$

These minimizations of first the s^2 coefficient and subsequently the s^4

coefficient reduce the tangent-plane distance to a function of the single distance parameter s , i.e.,

$$F(s) = bs^2 + cs^3 + d^*s^4 + \dots \quad (41)$$

with

$$d^* = d + (1/2)(\mathbf{w}^*)^T \mathbf{r} \quad (42)$$

At the critical point $b = c = 0$, and the critical point is locally stable provided that $d^* > 0$. If d^* equals zero, higher-order terms must be evaluated to determine whether or not the system is stable. Stability when $d^* = 0$ requires that the coefficient of s^5 , which depends on \mathbf{u} and \mathbf{w}^* only, must equal zero, and that the minimal value of the coefficient of s^6 is at least nonnegative. This coefficient depends on \mathbf{q} , and its minimal value is found by solving a set of linear equations similar to eqn. (36) for \mathbf{q} . Global stability requires that $F(\mathbf{Y})$ be nonnegative for arbitrary \mathbf{Y} , and the question of global stability cannot be resolved by expansions from $\mathbf{Y} = \mathbf{z}$. It is worthwhile noticing that $d^* \leq d$, where the equality sign holds only provided that \mathbf{r} is parallel to \mathbf{u} (in which case \mathbf{w}^* equals $\mathbf{0}$). Positiveness of d is therefore not a sufficient condition for local stability.

PHASE BOUNDARY IN THE CRITICAL REGION

In the immediate vicinity of a locally stable critical point, b and c are both small relative to d^* . At a point $(T, P) = (T_c + \Delta T, P_c + \Delta P)$ on the phase boundary close to the critical point, the coefficients b and c must have values such that $F(s)$ has a minimum at, say $s = \delta$, with $F(\delta) = 0$. This requires that

$$(dF/ds)_{s=\delta} = \delta(2b + 3c\delta + 4d^*\delta^2) = 0 \quad (43)$$

and

$$F(\delta) = \delta^2(b + c\delta + d^*\delta^2) = 0 \quad (44)$$

from which,

$$c = -2d^*\delta$$

$$b = d^*\delta^2 \quad (45)$$

In addition, for b and c ,

$$b(T_c + \Delta T, P_c + \Delta P) = b(T_c, P_c) + b_T \Delta T + b_P \Delta P = b_T \Delta T + b_P \Delta P \quad (46)$$

$$c(T_c + \Delta T, P_c + \Delta P) = c(T_c, P_c) + c_T \Delta T + c_P \Delta P = c_T \Delta T + c_P \Delta P \quad (47)$$

Combination of eqns. (45)–(47) then yields

$$\Delta T = \alpha_T \delta$$

$$\Delta P = \alpha_P \delta \quad (48)$$

with

$$\begin{aligned}\alpha_T &= 2d^*b_p/(b_Tc_p - b_pc_T) \\ \alpha_p &= -2d^*b_T/(b_Tc_p - b_pc_T)\end{aligned}\quad (49)$$

for δ sufficiently small. The composition of the equilibrium phase is given by

$$Y_i \approx z_i + v_i u_i \delta$$

or

$$\ln K_i = \ln(Y_i/z_i) = \delta u_i/v_i \quad (50)$$

Equations (48)–(50) provide a parametric relation between first-order variations in temperature, pressure and composition along the phase boundary in the vicinity of the critical point.

It can finally be mentioned that alternative transformations of the independent variables lead to identical results. Michelsen (1982a) used

$$Y_i = (v_i + X_i/2)^2 \quad (51)$$

and another possibility is

$$Y_i = z_i \exp(X_i/v_i) \quad (52)$$

Rather than working with the modified tangent-plane distance, the original tangent-plane distance

$$f(\mathbf{y}) = \sum_i y_i [\ln y_i + \ln \phi_i(\mathbf{y}) - \ln z_i - \ln \phi_i(\mathbf{z})] = F(\mathbf{y}) - 1 + \sum_i y_i \quad (53)$$

can also be used. The modifications required, which of course do not affect the constants of eqn. (41), are described in Appendix B.

To illustrate the nature of tangent-plane-distance surfaces in the critical region, a contour plot of $f(\mathbf{y})$ is given in Fig. 1(a) for a mixture containing 70% CH_4 , 15% CO_2 and 15% H_2S at $T = 225.02$ K, $P = 70.49$ atm., using the Soave–Redlich–Kwong equation of state (Soave, 1972). This corresponds to a point very close to the phase boundary, the nontrivial minimum having a value close to zero. The contours are replotted in Fig. 1(b) using “eigenvector coordinates” as described in Appendix B, where s_1 corresponds to the distance s along the eigenvector \mathbf{u} . The curve $\mathbf{X} = s\mathbf{u} + s^2\mathbf{w}^*$ is also shown in Fig. 1(b). Notice that this curve passes the saddle point and the nontrivial minimum at very close distances, while the variation of f along the s_1 axis just barely reveals the presence of an additional minimum. The critical point for this mixture is at $T = 232.15$ K, $P = 77.81$ atm.

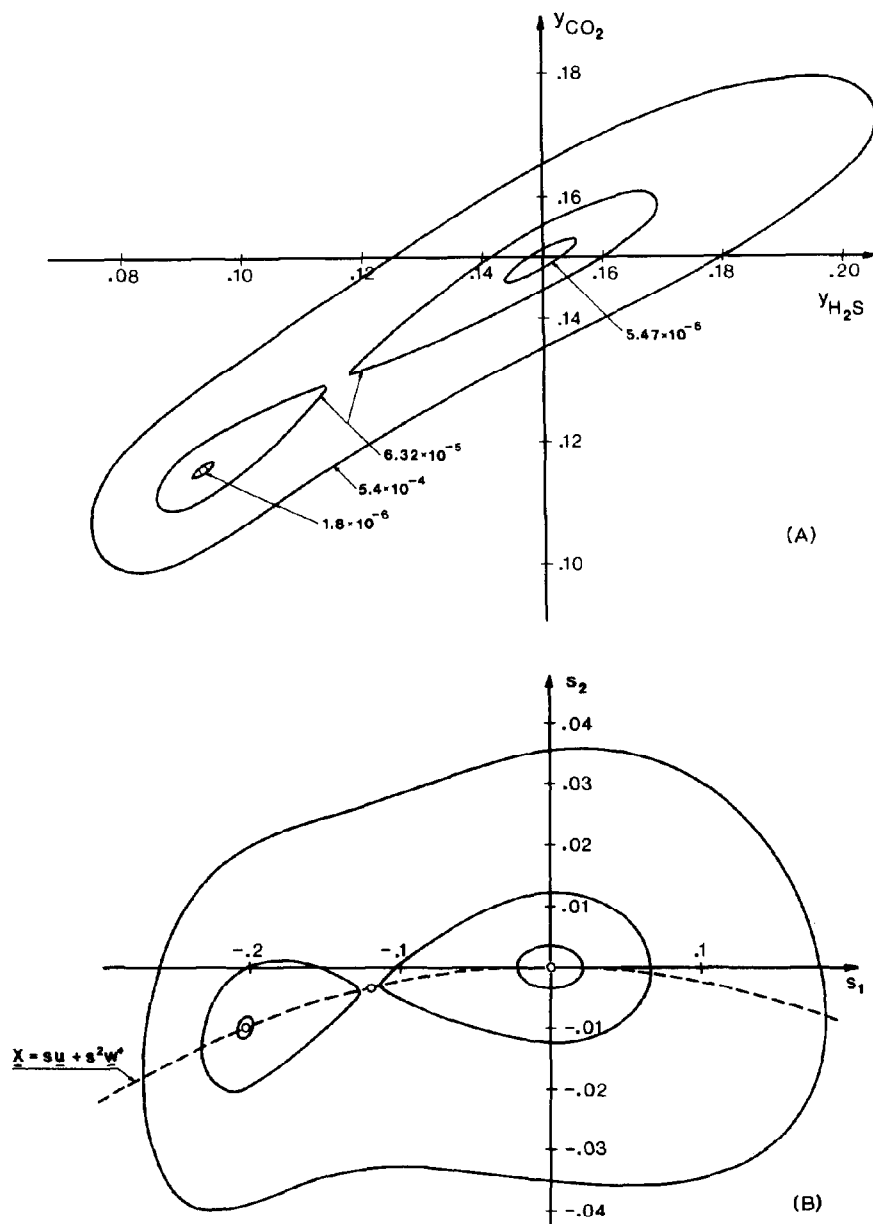


Fig. 1. Tangent-plane distance for a ternary mixture of CH_4 , CO_2 and H_2S for a point close to the phase boundary: (a) contour plot of $f(y)$; (b) plot in "eigenvector coordinates" (Appendix B).

STABILITY ANALYSIS

The stability investigation used by Michelsen (1982a) for nearly critical conditions closely resembles the approach described here. In particular, the suggestion of supplementing the search in the primary direction (along \mathbf{u}) by a correction step in an orthogonal direction corresponds to the present calculation of \mathbf{w}^* . A "stability indicator" can be deduced from eqns. (47) and (48). The existence of a nontrivial minimum requires that

$$9c^2 - 32bd^* \geq 0 \quad (54)$$

and a negative value at the minimum is found provided that

$$c^2 - 4bd^* > 0 \quad (55)$$

Local stability can thus be expected (for positive b and d^*) if eqn. (55) is not violated. This result is stronger than the usual criterion, $b > 0$, but it is only approximate, since it requires that higher-order terms are negligible.

CRITICAL-REGION PHASE BEHAVIOUR IN THE TWO-PHASE REGION

Inside the phase boundary, two phases of compositions $\mathbf{y}^{(1)}$ and $\mathbf{y}^{(2)}$ and in amounts of β and $(1 - \beta)$ moles per mole of feed will form such that the total Gibbs energy of the system is at a minimum. Michelsen (1982a, eqn. 8) showed that the change in Gibbs energy is related to the tangent-plane distances at compositions $\mathbf{y}^{(1)}$ and $\mathbf{y}^{(2)}$ by

$$\begin{aligned} \Delta G/RT &= \beta f(\mathbf{y}^{(1)}) + (1 - \beta)f(\mathbf{y}^{(2)}) \\ &= \beta F(\mathbf{y}^{(1)}) + (1 - \beta)F(\mathbf{y}^{(2)}) \end{aligned} \quad (56)$$

We define a composition-difference vector by

$$\Delta = \mathbf{y}^{(1)} - \mathbf{y}^{(2)}, \quad \sum_i \Delta_i = 0 \quad (57)$$

yielding

$$\begin{aligned} \mathbf{y}^{(1)} &= \mathbf{z} + (1 - \beta)\Delta \\ \mathbf{y}^{(2)} &= \mathbf{z} - \beta\Delta \end{aligned} \quad (58)$$

to satisfy the material-balance constraints. The objective is to select β and Δ such that eqn. (56) is minimized.

Again we select new variables $X_i = \Delta_i/v_i$ corresponding to the transformation used in eqn. (4). In the critical region the concentration difference will

be small, and $F(\mathbf{y}^{(1)})$ and $F(\mathbf{y}^{(2)})$ can be expanded in power series in \mathbf{X} from $\mathbf{X} = \mathbf{0}$, in analogy with eqn. (30):

$$\begin{aligned} \frac{\Delta G}{RT} = & (1/2)\beta(1-\beta) \sum_{i,j} B_{ij} X_i X_j + (1/6)\beta(1-\beta)(1-2\beta) \sum_{i,j,k} C_{ijk} X_i X_j X_k \\ & + (1/24)\beta(1-\beta)(1-3\beta+3\beta^2) \sum_{i,j,k,l} D_{ijkl} X_i X_j X_k X_l + \dots \end{aligned} \quad (59)$$

The X_i must now satisfy $\sum v_i X_i = 0$. \mathbf{X} may be expanded in a power series in the distance parameter s , as

$$\mathbf{X} = s\mathbf{u} + s^2\mathbf{w} + \dots \quad (60)$$

with

$$\mathbf{u}^T \mathbf{u} = 1, \mathbf{u}^T \mathbf{w} = 0, \mathbf{u}^T \mathbf{v} = \mathbf{w}^T \mathbf{v} = 0 \quad (61)$$

in order to satisfy the summation constraint for \mathbf{X} . Substituting eqn. (60) into eqn. (59) and collecting terms in equal powers of s yields

$$\Delta G/RT = s^2 \kappa_2(\beta, \mathbf{u}) + s^3 \kappa_3(\beta, \mathbf{u}) + s^4 \kappa_4(\beta, \mathbf{u}, \mathbf{w}) + \dots \quad (62)$$

Next, \mathbf{u} is selected to minimize κ_2 and subsequently \mathbf{w} to minimize κ_4 . The development follows closely that for the stability analysis, the essential differences being the presence of the parameter β and the need to satisfy the summation constraint. As shown in Appendix B, this constraint is without notable influence on the final result given below. It is again found that \mathbf{u} is the eigenvector of \mathbf{B} corresponding to λ_{\min} , and that \mathbf{w} can be taken as

$$\mathbf{w} = (1 - 2\beta)\mathbf{w}^* \quad (63)$$

where \mathbf{w}^* is the solution of eqn. (36).

Substituting \mathbf{u} , \mathbf{w} and the coefficients b , c , d and d^* from the stability analysis finally yields

$$\begin{aligned} \Delta G/RT = & \beta(1-\beta) \{ bs^2 + c(1-2\beta)s^3 \\ & + s^4 [(1-2\beta)^2(d^* - d) + (1-3\beta+3\beta^2)d] \} + \dots \end{aligned} \quad (64)$$

that is, an expression which involves only s and β as independent variables. These are next determined from the requirement that ΔG is at a minimum, or

$$\frac{\partial}{\partial s}(\Delta G/RT) = \frac{\partial}{\partial \beta}(\Delta G/RT) = 0 \quad (65)$$

Assume that the minimum is found at $s = \delta$. Then, the above conditions (eqn. (65)) yield

$$c = -2d^*(1-2\beta)\delta \quad (66)$$

$$b = [d^*(1-2\beta)^2 - 2d\beta(1-\beta)]\delta^2 \quad (67)$$

Combining these relations with the temperature and pressure derivatives of b and c at the critical point (eqns. (46) and (47)), the temperature and pressure variations are obtained as

$$\Delta T = T - T_c = \alpha_T(1 - 2\beta)\delta \quad (68)$$

$$\Delta P = P - P_c = \alpha_P(1 - 2\beta)\delta \quad (69)$$

together with eqn. (50) for the composition variation.

For the phase line $\beta = 0.5$, ΔT and ΔP become proportional to δ^2 when the critical point is approached. The proportionality constants can be derived, including the s^5 term in the expansion represented by eqn. (4), the result being

$$\begin{pmatrix} \Delta T \\ \Delta P \end{pmatrix}_{\beta=0.5} = -(1/2)\delta^2 \begin{pmatrix} b_T & b_P \\ c_T & c_P \end{pmatrix}^{-1} \begin{pmatrix} d \\ e \end{pmatrix} \quad (70)$$

with

$$e = (1/120)(d^5 F_1/ds^5) + (1/2) \sum_{i,j,k,l} D_{ijkl} w_i^* u_j u_k u_l \quad (71)$$

Finally, eqns. (66) and (67) can be used to calculate approximate values of the phase split for a point (T, P) in the two-phase region and close to the critical point. Evaluating b , c , d and d^* at (T, P, z) , elimination of δ from eqns. (66) and (67) yields

$$(1 - 2\beta)^{-2} = 1 + 2(d^*/d)(1 + 4bd^*/c^2) \quad (72)$$

Subsequently, δ can be calculated from eqn. (66) and the K factors from eqn. (50).

Note that, in accordance with the stability criterion given as eqn. (57), a value of β in the range $0 < \beta < 1$ requires that $c^2 - 4bd^* > 0$. The results for the two-phase region are thus fully consistent with the results for the phase boundary.

NUMERICAL EXAMPLE

The first-order approximations derived in this work are here compared with the results of direct phase equilibrium calculations for a seven-component natural-gas mixture described by Michelsen (1982a). The relevant thermodynamic properties are evaluated from the Soave-Redlich-Kwong equation of state (Soave, 1972). The mixture composition and the elements u_i/v_i describing the K -factor variation at the critical point ($T_c = 203.12$ K, $P_c = 58.11$ atm.) are given in Table 1. The relevant expansion coefficients at the critical point are listed in Table 2.

TABLE 1

Composition and principal eigenvector u at critical point for a seven-component mixture

Component	Mole fraction	$u_i z_i^{-1/2}$
C_1	0.9430	-0.16
C_2	0.0270	2.66
C_3	0.0074	4.79
$n-C_4$	0.0049	6.87
$n-C_5$	0.0027	8.99
$n-C_6$	0.0010	11.04
N_2	0.0140	-1.78

TABLE 2

Expansion coefficients and their temperature and pressure derivatives at the critical point for mixture given in Table 1

Coefficient	Value
b_T	-0.0618
b_P	0.0504
c_T	0.1537
c_P	-0.2105
d	2.058
d^*	0.943

TABLE 3

Predicted and calculated temperature and pressure variations along the $\beta = 0.5$ line for mixture given in Table 1

δ	$(T - T_c)/\delta^2$	$(P - P_c)/\delta^2$
0.10	-38.6	-66.7
0.05	-37.3	-65.9
0.02	-36.8	-65.6
Predicted	-37.0	-65.7

TABLE 4

Predicted and calculated phase distributions in the critical region for mixture given in Table 1

Specified values		Predicted from eqn. (71)	
β	δ	β	δ
0.20	0.05	0.30	0.039
0.20	0.02	0.24	0.017
0.20	0.01	0.22	0.0093
0.20	0.005	0.21	0.0048
0.5	0.05	0.39	0.054
0.5	0.02	0.46	0.0202
0.5	0.01	0.48	0.010
0.5	0.005	0.49	0.005

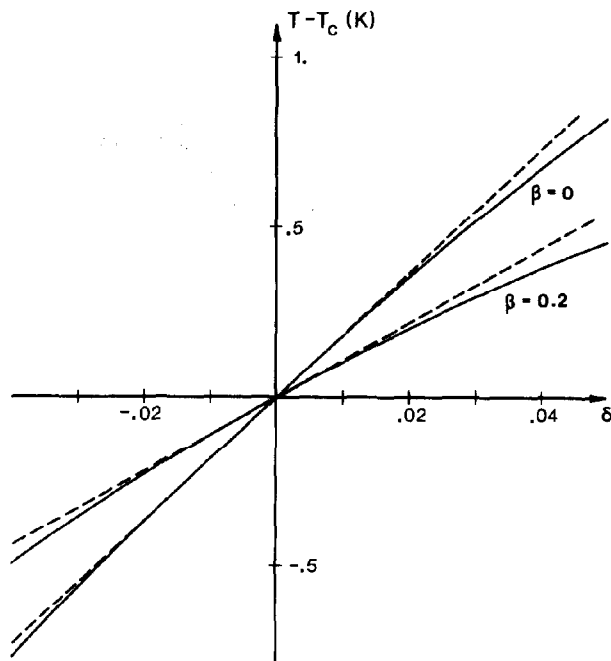


Fig. 2. $T - T_c$ versus δ for seven-component mixture given in Table 1: full lines, calculated results; dotted lines, results predicted using eqn. (48).

Figure 2 shows $T - T_c$ as a function of the distance parameter δ (calculated as $\delta = \sum_i u_i v_i \ln K_i$) for phase fractions $\beta = 0$ and $\beta = 0.2$. The agreement with eqn. (48) (dotted line) is perfect near $\delta = 0$ and quite good over a fairly wide range. Table 3 shows values of $T - T_c$ and $P - P_c$ as a function of δ along the line $\beta = 0.5$. The agreement with the prediction is excellent.

Finally, a comparison of the phase splits predicted by eqn. (72) with actual phase splits at the specified conditions is given in Table 4 for a number of points in the two-phase region. Although the predictions are qualitatively correct, substantial deviations are noted unless δ is very small.

CONCLUSION AND DISCUSSION

The present procedure for the calculation of critical points and of the phase boundary in the vicinity of the critical point is of particular use in connection with complete phase-boundary calculations as described by Michelsen (1980). This procedure for constructing the phase boundary is capable of passing the critical point, but numerical problems can be severe in

the vicinity of the latter, since the determinant of the Jacobian matrix is inversely proportional to the fourth power of the distance from the critical point.

Combination of Michelsen's marching procedure with the present direct calculation of the critical point and the associated derivatives required for phase-envelope construction obviates the need to calculate points on the phase boundary close to the critical point. The present procedure also allows calculation of the phase boundary starting from a critical point. Finally, the procedure provides a first estimate of phase composition and phase amounts for flash calculations at specified T and P in the critical region, based on properties derived for the feed composition only.

For stand-alone calculations of critical points, good initial estimates of the critical temperature and pressure are needed. A procedure similar to that described here using temperature and total volume as the independent variables and based on a tangent plane in Helmholtz energy is easily derived, and preliminary investigations indicate that such a procedure combines the economy of the present method with the reliability and insensitivity to initial estimates of the method of Heidemann and Khalil.

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LIST OF SYMBOLS

a, b, c, d, e	expansion coefficients for tangent-plane distance
A, B, C, D	coefficients of matrices of partial derivatives for tangent-plane distance
\mathbf{B}	matrix of second derivatives
f	original tangent-plane distance
F	modified tangent-plane distance
\mathbf{g}	gradient vector (eqn. (2))
$\Delta G, G$	molar Gibbs energy
\mathbf{h}	solution vector (eqn. (24))
i, j, k, l	component indices
K_i	Equilibrium factor for component i
n	mole number
N	number of components in mixture
$P, \Delta P$	pressure, pressure difference
P_c	critical pressure
\mathbf{q}	expansion vector (eqn. (31))

Q	scalar multiplier (eqn. (24))
\mathbf{r}	vector defined in eqn. (35)
R	gas constant
s	distance parameter
$T, \Delta T$	temperature, temperature difference
\mathbf{u}	eigenvector of \mathbf{B}
\mathbf{v}	vector with i th element $z_i^{1/2}$
\mathbf{w}, \mathbf{w}^*	expansion vectors (eqns. (31) and (36))
\mathbf{X}	vector of deviation variables
$y^{(1)}, y^{(2)}$	phase mole fractions
\mathbf{Y}	trial phase mole numbers
\mathbf{z}	vector of feed mole fractions
α_T, α_P	coefficients of temperature and pressure variation (eqn. (49))
β	phase fraction
γ	vector defined in eqn. (23)
δ	distance parameter (value of s at minimum)
ϵ	increment for numerical differentiation
$\kappa_2, \kappa_3, \kappa_4$	coefficients of Gibbs-energy expansion
λ_{\min}	eigenvalue of \mathbf{B}
ϕ_i	fugacity coefficient for component i

Superscripts

T	vector transpose
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Subscripts

P	partial derivative with respect to pressure
T	partial derivative with respect to temperature

APPENDIX A: NUMERICAL SOLUTION OF HOMOGENEOUS ALGEBRAIC EQUATIONS

This appendix describes briefly the solution procedure for a set of N linear algebraic equations of the form

$$\mathbf{B}\mathbf{x} = \mathbf{a} \quad (\text{A1})$$

where the matrix of coefficients \mathbf{B} and the augmented matrix (\mathbf{B}, \mathbf{a}) are both of rank $N - 1$, the objective being to determine a particular solution, $\mathbf{x} = \mathbf{h}$. Such equations are encountered in the calculation of the eigenvector derivatives \mathbf{u}_P and \mathbf{u}_T (eqn. (23)) and of the correction vector \mathbf{w}^* (eqn. (36)).

Since the N equations are known to be linearly dependent, a simple

procedure is simply to take $x_N = 0$ and delete the last equation from the set. This yields the reduced system

$$\mathbf{B}'\mathbf{x}' = \mathbf{a}' \quad (\text{A2})$$

where \mathbf{B}' is the upper $(N-1) \cdot (N-1)$ submatrix of \mathbf{B} , and \mathbf{a}' contains the first $N-1$ elements of \mathbf{a} . Provided that a triangular decomposition of \mathbf{B} is available ($\mathbf{B} = \mathbf{LU}$ with \mathbf{L} unit lower triangular), an even simpler procedure is available, where

$$\mathbf{U}\mathbf{x} = \mathbf{L}^{-1}\mathbf{a} = \mathbf{b} \quad (\text{A3})$$

where (in exact arithmetic) U_{NN} and b_N are both equal to zero. Taking x_N equal to zero results in a reduced system where the matrix of coefficients \mathbf{U}' is triangular.

In solving eqn. (23),

$$(\mathbf{B} - \lambda_{\min}\mathbf{I})\mathbf{u}_p = \mathbf{v} \quad (\text{A4})$$

the triangular decomposition of \mathbf{B} is available from the eigenvalue calculation, while exact evaluation of \mathbf{u}_p would require the triangular factors of $\mathbf{B} - \lambda_{\min}\mathbf{I}$. To avoid renewed factorization, the small term $\lambda_{\min}\mathbf{I}$ in eqn. (A4) is neglected, the equation to be solved becoming

$$\mathbf{B}\mathbf{u}_p = \mathbf{v} \quad (\text{A5})$$

or

$$\mathbf{U}\mathbf{u}_p = \mathbf{L}^{-1}\mathbf{v} \quad (\text{A6})$$

where the procedure above (taking $(\mathbf{u}_p)_N = 0$) is used even though U_{NN} and the last element of $\mathbf{L}^{-1}\mathbf{v}$ are both nonzero. It can be shown that the approximations introduced in this calculation of \mathbf{u}_p (and \mathbf{u}_T) do not degrade the performance of the Newton–Raphson iteration.

APPENDIX B: RELATION BETWEEN MODIFIED AND ORIGINAL TANGENT-PLANE CRITERIA

The advantage of using the modified tangent-plane criterion (eqn. (1)) is the convenience that the composition variables Y_i can be treated as fully independent. The original tangent-plane criterion (eqn. (53)) requires that the y_i satisfy the constraint $\sum_i y_i = 1$. In terms of the new independent variables X_i , this requirement yields

$$\mathbf{X}^T \mathbf{v} = 0 \quad (\text{B1})$$

with $v_i = z_i^{1/2}$. The transformation to \mathbf{X} as the vector of independent variables consists of a translation of the coordinate system followed by a scaling such that contours of constant F close to $\mathbf{X} = \mathbf{0}$ become hyperspheres for an ideal mixture.

We shall in addition perform a rotation of the coordinate system using an orthogonal transformation

$$\mathbf{X} = \mathbf{U}\mathbf{s} \quad (\text{B2})$$

where \mathbf{U} is the matrix of eigenvectors of \mathbf{B} ,

$$\mathbf{U}^T \mathbf{B} \mathbf{U} = \mathbf{\Lambda}, \quad \mathbf{U}^T = \mathbf{U}^{-1} \quad (\text{B3})$$

with $\mathbf{\Lambda}$ being the diagonal eigenvalue matrix of \mathbf{B} . Discarding terms of the third and higher orders in \mathbf{X} , the contours are now given by

$$F(\mathbf{X}) = (1/2)\mathbf{X}^T \mathbf{B} \mathbf{X} = (1/2)\mathbf{s}^T \mathbf{U}^T \mathbf{B} \mathbf{U} \mathbf{s} = (1/2)\mathbf{s}^T \mathbf{\Lambda} \mathbf{s}$$

or

$$F(\mathbf{s}) = (1/2) \sum_i \lambda_i s_i^2 \quad (\lambda_i = \Lambda_{ii}) \quad (\text{B4})$$

i.e., contours of constant F become hyperellipsoids in the s coordinate system provided that all λ_i are positive.

Let the i th eigenvector of \mathbf{B} , that is, the i th column of \mathbf{U} , be \mathbf{u}_i . Of the N eigenvectors, two are of particular interest. The first is the eigenvector \mathbf{u}_1 corresponding to the smallest eigenvalue $\lambda_1 = \lambda_{\min}$ (that is, our previous \mathbf{u}), and the second is the eigenvector $\mathbf{u}_N = \mathbf{v}$ with eigenvalue $\lambda_N = 1$. That \mathbf{v} is an eigenvector with an eigenvalue of 1 follows from

$$\begin{aligned} \sum_i B_{ij} v_j &= \sum_i z_j^{1/2} \left[\delta_{ij} + z_i^{1/2} z_j^{1/2} (\partial \ln \phi_i / \partial n_j)_z \right] \\ &= z_i^{1/2} + z_i^{1/2} \sum_j z_j (\partial \ln \phi_i / \partial n_j)_z = z_i^{1/2} = v_i \end{aligned}$$

or $\mathbf{B}\mathbf{v} = \mathbf{v}$. From the orthogonality of eigenvectors for a symmetric matrix,

$$\mathbf{v}^T \mathbf{u}_i = 0, \quad i \neq N \quad (\text{B5})$$

and hence vectors \mathbf{X} which are selected as linear combinations of the first $N - 1$ columns of \mathbf{u} all satisfy eqn. (B1). The function $F_1(s)$ uses $\mathbf{X} = s\mathbf{u}$, and hence is identical for the modified and original criteria.

A minor difference is noted in the minimization of the coefficient of s^4 in eqn. (35), where the minimizer for the original tangent-plane criterion, which we shall call $\hat{\mathbf{w}}$, must satisfy the additional constraint $\mathbf{v}^T \hat{\mathbf{w}} = 0$. Straightforward but fairly extensive derivations reveal that

$$\hat{\mathbf{w}} = \mathbf{w}^* - b\mathbf{v} \quad (\text{B6})$$

and that the corresponding coefficient \hat{d} is given by

$$\hat{d} = d^* + b^2/2 \quad (\text{B7})$$

At the critical point b equals zero, and within the region where the present

expansions are valid, b is small. The differences between the modified and original tangent-plane criteria are thus without significance for the results given here.

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