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On the Calculation of Critical Points by the Method of Heidemann and Khalil

Brian E. Eaton

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On the Calculation of Critical Points by the Method of Heidemann and Khalil

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ON THE CALCULATION OF CRITICAL POINTS BY THE METHOD OF HEIDEMANN AND KHALIL Brian E. Eaton

The formulation of critical point criteria by Heidemann and Khalil is analyzed and contrasted with the original formulation of Gibbs. An extension to the solution technique originally used by Heidemann and Khalil, and later improved by Michelsen and Heidemann, is presented along with its detailed implementation for a general two-constant cubic equation of state. Finally, FORTRAN software developed for these computations is carefully documented.

Key words: algorithm; critical locus; Helmholtz free energy; mixtures; Peng-Robinson equation of state; thermodynamics

1. Introduction

The topic of this technical note is the computation of critical points in multicomponent mixtures using equations of state. The thermodynamic conditions for a critical point were orginally formulated by Gibbs \3}, but because of their complexity, they were not solved using equations of state for multicomponent mixtures for another 100 years. Peng and Robinson \10} computed critical points in multicomponent mixtures using their cubic equation of state and the conditions for criticality exactly as given by Gibbs \3}, i.e., Gibbs' equations (206-208). Shortly thereafter, Heidemann and Khalil \4} proposed an alternative computational procedure based on a mathematical reformulation of the original conditions of Gibbs. The computational procedure of Heidemann and Khalil is substantially more efficient than that employed by Peng and Robinson.

The purpose of this note is twofold. First, the criteria for a critical point will be examined in some detail. Emphasis is placed on elucidating the similarities and differences between the two mathematical formulations mentioned above. Second, a description of Heidemann and Khalil's solution technique using a general two-constant cubic equation of state is presented along with an extension which may lead to a more efficient iteration on the volume. In the final section, the FORTRAN software developed for the computations is carefully documented.

2. Conditions for the Local Stability of a Homogeneous Phase

To formulate the mathematical conditions for a critical point, we begin by considering the stability of a homogeneous phase with respect to continuous change. Implicit in this statement is the differentiation between an arbitrarily small (continuous) change in a phase and a change which involves the appearance of a new phase (discontinuous). A phase may be stable with regard to the former type of change and unstable with regard to the latter (i.e., a metastable state). Stability with respect to continuous changes is referred to as local stability and that with respect to discontinuous changes is termed global stability.

Thermodynamic stability theory rests upon a hypothesis which, in its original form as stated by Gibbs, does not lead unambiguously to intuitive concepts and mathematical formalism; an excerpt from Tisza \14} (p. 41) clarifies this point:

Gibbs stated the extremum principle in two versions: in an isolated system the entropy tends to a maximum at constant energy, or alternatively, the energy tends to a minimum at constant entropy. Although these statements undoubtedly express important truths, they lack precision to the point of being paradoxical. If an isolated system is not in equilibrium, we can associate no entropy with it, and if it is in equilibrium, its entropy can no longer increase. Many authors have grappled with this dilemma until a satisfactory solution was found in terms of the composite system. Consider a system of two or more spatially disjoint parts separated by adiabatic partitions. After reaching equilibrium each part has a definite entropy, the sum of which is associated with the composite system. The relaxation of an internal constraint will, in general, trigger a process, namely the redistribution, say, of energy at constant volume,

$$(DU')_{V'} + (DU'')_{V''} = 0$$

leading to a new equilibrium with higher entropy. Here D denotes a finite change that actually takes place in the system and for which all the conservation laws and boundary conditions are satisfied. Thus the increase of entropy is perfectly well defined since it is associated with a transition from a more restricted to a less restricted equilibrium.

Development of the stability conditions from the extremum principles and the composite system concept summarized below can also be found in Tisza [14] and in Modell and Reid [8]. It is convenient to consider the results in terms of the energy rather than the entropy since the Legendre transforms of the energy result in the free energy expressions which are readily calculated using equations of state.

The extensive state of a system can be represented in terms of c + 2 variables, where c is the number of independent components,

$$U(S, V, n_1, ..., n_{c-1}, N);$$
 (2.1)

the internal energy (U) is a function of the entropy (S), volume (V), number of moles of component i (n_i) and the total number of moles (N). It is generally assumed that the stability of a system is an intrinsic property which does not depend on its size. This assumption is not universally valid: for example, it is not valid for small droplets, where surface tension effects are important, nor is it valid for large stars, where gravity must be taken into account. However, size dependent effects will not be considered here; hence, the size of the system will be fixed by holding, say, N constant. Variations in the energy are then expressed by

$$dU = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV + \sum_{i=1}^{C-1} \frac{\partial U}{\partial n_i} dn_i , \qquad (2.2)$$

where the variables held constant in the partial differentiations follow from the functional dependence expressed in (2.1). Introducing some additional nomenclature, we rewrite (2.2) as follows,

$$dU = \sum_{i=1}^{r} \frac{\partial U}{\partial X_{i}} dX_{i} = \sum_{i=1}^{r} U_{i} dX_{i} , \qquad (2.3)$$

where X_i is the ith component of the vector $X = [S, V, n_i, ..., n_{c-1}]^T$,

¢

$$U_i \equiv \frac{\partial U}{\partial X_i}$$
, and $r \equiv c + 1$.

The U_i represent the intensities of the system, that is U_i is the ith component of the vector $\underline{P} = [T, -p, \mu_1, \dots, \mu_{C-1}]^T$ where T is temperature, p is pressure, and μ_i is the chemical potential of mixture component i. The superscript T represents the transpose operation, i.e., \underline{X} and \underline{P} are column vectors.

The extremum principle is expressed as follows. Consider a composite system, the subsystems of which are identified by the superscripts α and β . The initial state, in which subsystems α and β are assumed to be in a state of unconstrained equilibrium (all the intensities in α equal the intensities of β), is characterized by

$$U^{\text{system}} = U^{\alpha} + U^{\beta} . \qquad (2.4)$$

The constraint that the composite system be isolated takes the form

$$X_{i}^{\alpha} + X_{i}^{\beta} = \text{const.}, \quad i = 1, ..., r$$
 (2.5)

and the relative sizes of α and β are specified by fixing the values N^{α} and N^{β}. The allowable virtual processes used to test the stability of the system can be visualized as an exchange of the quantities X₁ between the subsystems α and β subject to the constraints of (2.5). Thus, a virtual process, or a displacement from the equilibrium state, has the property that

$$\delta X_{i}^{\alpha} = -\delta X_{i}^{\beta}$$
, $i = 1, ..., r$ (2.6)

where the symbol δ denotes an arbitrarily small displacement. According to the energy extremum principle (as stated by Tisza), any virtual process which takes the composite system from an initially unconstrained equilibrium to a constrained equilibrium must result in a higher energy for the composite. The response of the system's energy to such virtual processes is expressed by a Taylor series expansion about the initial equilibrium state, i.e.,

$$\Delta U^{\text{system}} = \Delta U^{\alpha} + \Delta U^{\beta}$$

= $\delta U^{\alpha} + \frac{1}{2} \delta^{2} U^{\alpha} + \frac{1}{6} \delta^{3} U^{\alpha} + ...$ (2.7)
+ $\delta U^{\beta} + \frac{1}{2} \delta^{2} U^{\beta} + \frac{1}{6} \delta^{3} U^{\beta} + ...$

where

$$\delta U = \sum_{i=1}^{r} \frac{\partial U}{\partial X_{i}} \quad \delta X_{i} = \sum_{i=1}^{r} U_{i} Z_{i} , \qquad (2.8)$$

$$\delta^{2} U = \sum_{i,j=1}^{r} \frac{\partial^{2} U}{\partial X_{i} \partial X_{j}} \delta X_{i} \delta X_{j} = \sum_{i,j=1}^{r} U_{ij} Z_{i} Z_{j}, \qquad (2.9)$$

$$\delta^{3} U = \sum_{i,j,k=1}^{r} \frac{\partial^{3} U}{\partial X_{i} \partial X_{j} \partial X_{k}} \quad \delta X_{i} \delta X_{j} \delta X_{k} = \sum_{i,j,k=1}^{r} U_{ijk} Z_{i} Z_{j} Z_{k} , \quad (2.10)$$

$$U_i = \frac{\partial U}{\partial X_i}$$
, $U_{ij} = \frac{\partial^2 U}{\partial X_i \partial X_j}$, $U_{ijk} = \frac{\partial^3 U}{\partial X_i \partial X_j \partial X_k}$, and $Z_i = \delta X_i$.

Substituting (2.6, 2.8-10) into (2.7) gives

$$u^{\text{system}} = \sum_{i=1}^{r} (U_i^{\alpha} - U_i^{\beta}) Z_i^{\alpha} + \frac{1}{2} \sum_{i,j=1}^{r} (U_{ij}^{\alpha} + U_{ij}^{\beta}) Z_i^{\alpha} Z_j^{\alpha}$$

$$(2.11)$$

$$+ \frac{1}{6} \sum_{\substack{i,j,k=1}}^{r} (U_{ijk}^{\alpha} - U_{ijk}^{\beta}) Z_{i}^{\alpha} Z_{j}^{\alpha} Z_{k}^{\alpha} + \dots$$

Since α and β were initially in equilibrium, $U_i^{\alpha} = U_i^{\beta}$; thus the first order form is identically zero. The quadratic and cubic forms are simplified by the following consideration. Since the energy is represented by a first order homogeneous function,

$$U^{\alpha} (X_{1}^{\alpha}, X_{2}^{\alpha}, \dots, X_{r}^{\alpha}) = k U^{\beta} (X_{1}^{\beta}, X_{2}^{\beta}, \dots, X_{r}^{\beta})$$
(2.12)

where k is the ratio of the sizes of two systems which can be denoted by $N^{\alpha}/N^{\beta}.$ Also,

$$X_{i}^{\alpha} = \kappa X_{i}^{\beta} . \qquad (2.13)$$

The following relationships between the partial derivatives of U^{α} and U^{β} follow from differentiating (2.12) and making use of (2.13):

$$U_i^{\alpha} = U_i^{\beta} , \qquad (2.14)$$

$$k U_{ij}^{\alpha} = U_{ij}^{\beta} , \qquad (2.15)$$

$$\kappa^2 U^{\alpha}_{ijk} = U^{\beta}_{ijk} . \qquad (2.16)$$

Substituting into (2.11) gives

$$\Delta U_{\text{system}} = \frac{1+k}{2} \sum_{i,j=1}^{r} U_{ij}^{\alpha} Z_{i}^{\alpha} Z_{j}^{\alpha} + \frac{1-k^{2}}{6} \sum_{i,j,k=1}^{r} U_{ijk}^{\alpha} Z_{i}^{\alpha} Z_{j}^{\alpha} Z_{k}^{\alpha} + \dots \quad (2.17)$$

The extremum principle requires that for an initially stable system, all virtual processes must result in the change

Hence, the quadratic form, which dominates the expansion as the virtual displacements Z_i^{α} are made arbitrarily small, must be positive, i.e.,

$$\delta^2 U > 0 . \qquad (2.19)$$

In (2.19) we divided by the positive constant (1 + k)/2, and dropped the superscript α since it is irrelevant which of the subsystems is considered.

The limit of stability is determined by the condition

$$\delta^2 U = 0$$
 . (2.20)

This condition is of particular interest in this discussion because a critical point is a stable point on the stability limit. The stability of a state for which $\delta^2 U = 0$ is determined by the higher order forms. Consider the cubic form. If a virtual process exists such that $\delta^3 U > 0$, then because the cubic form is an odd function of Z_i , there also exists a process (- Z_i) for which $\delta^3 U < 0$. Therefore, the stability of a critical point requires that

$$\delta^3 U = 0$$
 and $\delta^4 U > 0$. (2.21)

In a pathological case where $\delta^4 U = 0$, a similar argument to that used for the cubic form would require that $\delta^5 U = 0$ and $\delta^6 U > 0$.

In fact, it is normal procedure when computing critical points to consider only the conditions $\delta^2 U = 0$ and $\delta^3 U = 0$, and to rely on experimental evidence to infer that a critical point actually exists (i.e., is stable).

Before moving on to alternative formulations of the stability conditions, there is one more point to be made concerning our composite system model. In the preceding derivation we found the relative sizes of the subsystems α and β , expressed by the variable k, to be irrelevant to the stability conditions. There is a special value of k, however, which adds valuable intuition about the kinds of virtual processes which may be used to determine stability.

Consider the case where one of the subsystems, β , say, becomes very large. In the limit as $N^{\beta} \rightarrow \infty$, $k \rightarrow 0$, and by eqs (2.15-16) the second and higher order derivatives of U^B go to zero. Recognizing that the second order derivatives of U are the same as the first order derivatives of the intensities, $U_{ij}^{\beta} = 0$ implies that the intensities of β remain constant during any virtual process. This corresponds to the concept of ideal reservoirs. For example, the temperature of a thermal reservoir remains constant when heat (entropy) is added to or removed from it. Thus, a composite system consisting of a subsystem under study and an ideal reservoir leads naturally to the consideration of virtual processes in which the intensities are held constant.

3. Alternative Formulations of the Conditions for a Critical Point

We will consider a critical point to be determined by the conditions

$$s^2 U = s^3 U = 0 . (3.1)$$

Reformulations will be considered first for the quadratic form and subsequently for the cubic form.

3.1 The Quadratic Form

A stable system is given by the condition $\delta^2 U > 0$; in other words the quadratic form is positive definite. We shall eventually find it useful to express the results concerning the positive definiteness of the quadratic form in terms of matrix notations. Hence, the notation is introduced here,

$$\delta^2 U \equiv \underline{Z}^T \underline{U} \underline{Z} , \qquad (3.2)$$

where Z is the column vector (δS , δV , δn_1 , ..., δn_{c-1})^T,

where

 $\delta^{2} U = U_{11} \eta_{1}^{2} + U_{22}^{(1)} \left[z_{2} + \frac{U_{23}^{(1)}}{U_{33}^{(1)}} z_{3} \right]^{2} + \left[U_{33}^{(1)} + \frac{(U_{23}^{(1)})^{2}}{U_{33}^{(1)}} \right] z_{3}^{2}$

or

where

 $\delta^{2}U = U_{11} \eta_{1}^{2} + U_{22}^{(1)} \eta_{2}^{2} + U_{33}^{(2)} Z_{3}^{2},$ (3.10)

Continuing to complete the square,

 $U_{33}^{(1)} \equiv U_{33} - \frac{U_{13}^2}{U_{11}}$.

 $U_{23}^{(1)} \equiv U_{23} - \frac{U_{12}U_{13}}{U_{11}},$ (3.7)

 $U_{22}^{(1)} \equiv U_{22} - \frac{U_{12}^2}{U_{14}}$

(3.5)

(3.6)

(3.8)

(3.9)

 $= U_{11} n_1^2 + U_{22}^{(1)} Z_2^2 + 2 U_{23}^{(1)} Z_2 Z_3 + U_{33}^{(1)} Z_3^2,$ (3.4)

$$\delta^{2} U = U_{11} \left[Z_{1} + \frac{1}{U_{11}} \left(U_{12} Z_{2} + U_{13} Z_{3} \right) \right]^{2} - \frac{1}{U_{11}} \left(U_{12} Z_{2} + U_{13} Z_{3} \right)^{2} + U_{22} Z_{2}^{2} + 2 U_{23} Z_{2} Z_{3} + U_{33} Z_{3}^{2} ,$$

$$(3.3)$$

The first step in writing the quadratic form for a binary system as a sum of squares is

 $\eta_1 = Z_1 + \frac{1}{U_{11}} (U_{12} Z_2 + U_{13} Z_3) ,$

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and T indicates the transpose operation. A common technique used to derive conditions which determine the definiteness of a quadratic form is to diagonalize U using orthogonal transformations. However, orthogonal transformations do not turn out to be very useful in thermodynamics because the variables do not readily admit the definition of a metric (see, for example, Weinhold [15]). The most useful procedure for diagonalizing \underline{U} , from the viewpoint of thermodynamics, makes use of the technique completing-the-square. The diagonalization of U and subsequent reformulations of the stability conditions will now be considered in some detail for a binary system.

U is a symmetric matrix of elements U =

$$\frac{\partial^2 U}{\partial X_i \partial X_j}$$

$$n_2 = Z_2 + \frac{U_{23}^{(1)}}{U_{22}^{(1)}} Z_3, \qquad (3.11)$$

$$U_{33}^{(2)} = U_{33}^{(1)} - \frac{(U_{23}^{(1)})^2}{U_{22}^{(1)}} .$$
(3.12)

Equation (3.10) implies that for $\delta^2 U$ to be positive definite, the conditions

$$U_{11}^{(0)} \equiv U_{11} > 0$$
, (3.13)

$$U_{22}^{(1)} > 0$$
, (3.14)

$$U_{33}^{(2)} > 0$$
, (3.15)

must be satisfied.

The first step toward reformulating the stability conditions is to recognize that in a stable system moving toward an unstable state, the first quantity which will go to zero, and thus indicate the limit of stability, is $U_{33}^{(2)}$. It is common to make use of this single condition when searching for the stability limit of a system of interest and to use intuition gained from experimental evidence to guarantee that the search is started from a stable state. This is a practical approach. The purpose of indicating the implicit assumptions normally made is that when working with equations of state and Newton-Raphson search techniques on the computer, we can unwittingly project the solution into a region where the lower order stability conditions are not met and hence produce incorrect results.

To prove that the condition $U_{33}^{(2)}$ is the first to go to zero, consider (3.6) and (3.12) which indicate a general recursion formula relating successive stability conditions and can be written as:

$$U_{kk}^{(k-1)} = U_{kk}^{(k-2)} - \frac{\left(U_{k(k-1)}^{(k-2)}\right)^{2}}{U_{(k-1)(k-1)}^{(k-2)}} .$$
(3.16)

Under the assumption that the system is initially stable, $U_{(k-1)(k-1)}^{(k-2)}$, $U_{kk}^{(k-1)}$, and, hence, $U_{kk}^{(k-2)}$ are all positive. If we let $U_{(k-1)(k-1)}^{(k-2)}$ go to zero, then assuming that $U_{kk}^{(k-2)}$ remains finite and $(U_{k(k-1)}^{(k-2)})^2$ does not go to zero, $U_{kk}^{(k-1)}$ must become negative, and, hence, have become zero before $U_{(k-1)(k-1)}^{(k-2)}$ reaches zero. Therefore, $U_{kk}^{(k-1)}$ will become zero before $U_{(k-1)(k-1)}^{(k-2)}$ does as the stability limit is approached.

If we assume that $U_{11}^{(0)} > 0$, and use the recursion formula (3.16), then by induction the condition which will go to zero first, and thus indicate the limit of stability, will be $U_{rr}^{(r-1)}$, where r equals the number of rows and columns in \underline{U} .

The fact that the stability limit is determined by the condition $U_{rr}^{(r-1)} = 0$ allows us to deduce something about the types of virtual processes which may be used to test stability. In our model of the composite system we have imagined virtual processes (\underline{Z}) as the exchange of extensive quantities X_i between the subsystems α and β . The diagonalization of the quadratic form for the binary system resulted in a transformation from the virtual processes (Z_1 , Z_2 , Z_3) to the processes (η_1 , η_2 , Z_3). In general, diagonalization will transform the processes (Z_1 , Z_2 , ..., Z_r) to the processes (η_1 , η_2 , ..., η_{r-1} , Z_r). Since the limit of stability is determined by the coefficient of Z_r , the virtual processes used to test for stability need only include the subset given by ($\eta_i = 0$ (i = 1, ..., r-1), Z_r). That is, we may arbitrarily set the variations represented by the η_i to zero. Let us clarify exactly what types of processes the η_i correspond to.

Consider the connection between variations in the extensive and intensive variables for a binary system, i.e.,

$$\begin{bmatrix} U_{SS} & U_{SV} & U_{Sn_1} \\ U_{VS} & U_{VV} & U_{Vn_1} \\ U_{n_1S} & U_{n_1}V & U_{n_1n_1} \end{bmatrix} \begin{bmatrix} \delta S \\ \delta V \\ \delta n_1 \end{bmatrix} = \begin{bmatrix} T_S & T_V & T_{n_1} \\ -P_S & -P_V & -P_{n_1} \\ \mu_{1S} & \mu_{1V} & \mu_{1n_1} \end{bmatrix} \begin{bmatrix} \delta S \\ \delta V \\ \delta n_1 \end{bmatrix} = \begin{bmatrix} \delta T \\ -\delta P \\ \delta \mu_1 \end{bmatrix}. (3.17)$$

A process at constant temperature implies that

$$U_{SS} \delta S + U_{SV} \delta V + U_{Sn_1} \delta n_1 = \delta T = 0, \qquad (3.18)$$

or, converting notations

$$U_{11} Z_1 + U_{12} Z_2 + U_{13} Z_3 = 0 , \qquad (3.19)$$

and, since $U_{11} > 0$ for a stable system, we divide by it to obtain

$$Z_{1} + \frac{1}{U_{11}} (U_{12} Z_{2} + U_{13} Z_{3}) = 0.$$
 (3.20)

Comparing (3.20) and (3.5) leads us to the conclusion that $\eta_1 = 0$ is equivalent to a virtual process at constant temperature.

Since the stability limit may be determined by using constant temperature processes, it is natural to reformulate the quadratic form in terms of the Helmholtz free energy, i.e.,

$$\delta^{2}A = \sum_{i,j=1}^{2} A_{ij} Z_{i}Z_{j}$$
 (3.21)

where

$$\underline{Z} = (\delta V, \delta n_1)^T . \qquad (3.22)$$

Diagonalizing leads to

$$\delta^2 A = A_{11} n_1^2 + A_{22}^{(1)} Z_2^2 . \qquad (3.23)$$

And the limit of stability is determined by

$$A_{22}^{(1)} = A_{22} - \frac{A_{12}^2}{A_{11}} = 0.$$
 (3.24)

The stability limit takes a simpler form in terms of A because the constant temperature constraint is implicit in A which is the first Legendre transform of U with respect to S.

Let us carry the present line of thought one step further. Consider virtual processes which occur at constant temperature and pressure. The constraints placed on the variations of the extensive variables are

$$\begin{array}{rclcrcrcrc} U_{11} & Z_{1} & + & U_{12} & Z_{2} & + & U_{13} & Z_{3} & = & \delta T & = & 0 \ , \\ \\ U_{21} & Z_{1} & + & U_{22} & Z_{2} & + & U_{23} & Z_{3} & = & -\delta p & = & 0 \ . \end{array}$$

Eliminating Z1 from these equations gives

$$Z_{2} + \frac{U_{23} - \frac{U_{12} U_{13}}{U_{11}}}{U_{22} - \frac{U_{12}^{2}}{U_{11}}} Z_{3} = 0.$$
(3.25)

Comparing (3.25) and (3.11) shows that $n_2 = 0$ is equivalent to a process at constant temperature and pressure. Hence, the stability conditions can be expressed in the Gibbs free energy formulation, i.e.,

$$\delta^2 G = G_{11} Z_1^2 , \qquad (3.26)$$

where

$$Z_1 = \delta n_1$$
.

The limit of stability is given by the condition

$$G_{11} = 0$$
 (3.27)

For multicomponent mixtures we can generalize the conditions for the limit of stability as follows. In the energy representation,

$$U_{rr}^{(r-1)} = 0$$
 (3.28)

Considering virtual processes at constant T leads to

$$A_{(r-1)(r-1)}^{(r-2)} = 0 , \qquad (3.29)$$

and considering processes at constant T and p leads to

$$G_{(r-2)(r-2)}^{(r-3)} = 0$$
 (3.30)

Beyond this point we run out of commonly used symbols to represent the Legendre transforms of U, hence, the notation [Uⁱ] is introduced to represent the ith Legendre transform of U. Considering processes at constant T, p, μ_1 leads to

$$\begin{bmatrix} U^3 \end{bmatrix}_{(r-3)(r-3)}^{(r-4)} = 0 ; \qquad (3.31)$$

and considering processes where r-1 intensities are held constant, i.e., constant T, p, $\mu_1,$..., $\mu_{c-2},$ leads to

$$\begin{bmatrix} U^{r-1} \end{bmatrix}_{11}^{(0)} = 0 . \tag{3.32}$$

There are r equivalent formulations of the stability conditions for the particular ordering of independent variables we have chosen. Many more formulations are possible by taking different permutations of the order S, V, n_1 , ..., n_{c-1} . Of all possible formulations, there is really only one which interests us here; that is the formulation in terms of the Helmholtz free energy because most equations of state are written with T, V, n_1 , ..., n_c as the independent variables.

In addition to reformulating the stability conditions in terms of the Legendre transforms of the energy, there is another important reformulation which we consider now. As before, the motivation will come from working with the specific example of the binary system.

Consider the stability conditions given in eqs (3.13-15). The first condition can be trivially rewritten

$$U_{11}^{(0)} = U_{11} = \Delta_1,$$
 (3.33)

where Δ_1 is the first discriminant of the matrix \underline{V} . The mth discriminant of a matrix is the determinant of the submatrix obtained by deleting all elements which do not simultaneously lie in the first m rows and columns (see, for example, Hildebrand, p. 52).

The second condition can be rewritten,

$$U_{22}^{(1)} = \frac{1}{U_{11}} (U_{11} U_{22} - U_{12}^2)$$
(3.34)

or, due to the symmetry of U,

$$U_{22}^{(1)} = \frac{1}{U_{11}} \begin{vmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{vmatrix} = \frac{\Delta_2}{\Delta_1} .$$
(3.35)

The third condition can be rewritten,

$$U_{33}^{(2)} = (U_{33} - \frac{U_{13}^2}{U_{11}}) - \frac{U_{23} - \frac{U_{12} - U_{13}}{U_{11}}^2}{U_{22} - \frac{U_{12}^2}{U_{11}}}, \qquad (3.36)$$

$$= \frac{1}{(U_{11}U_{22} - U_{12}^2)} \frac{(U_{11}U_{22} - U_{12}^2)(U_{11}U_{33} - U_{13}^2) - (U_{11}U_{23} - U_{12}U_{13})^2}{U_{11}}, \quad (3.37)$$

$$U_{33}^{(2)} = \frac{\Delta_3}{\Delta_2} . \tag{3.38}$$

The quadratic form for a binary system can then be written,

$$\delta^{2} U = \Delta_{1} n_{1}^{2} + \frac{\Delta_{2}}{\Delta_{1}} n_{2}^{2} + \frac{\Delta_{3}}{\Delta_{2}} Z_{3}^{2} , \qquad (3.39)$$

and the condition for the stability limit translates into

$$\Delta_3 = 0$$
 . (3.40)

For the binary system, \underline{U} is a 3 x 3 matrix, hence (3.40) becomes

$$\Delta_3 = \det \left| \underbrace{\underline{U}}_{\underline{a}} \right| = 0 . \tag{3.41}$$

In general,

$$\delta^{2} U = \Delta_{1} n_{1}^{2} + \frac{\Delta_{2}}{\Delta_{1}} n_{2}^{2} + \frac{\Delta_{3}}{\Delta_{2}} n_{3}^{2} + \dots + \frac{\Delta_{r-1}}{\Delta_{r-2}} n_{r-1}^{2} + \frac{\Delta_{r}}{\Delta_{r-1}} Z_{r}^{2}, \qquad (3.42)$$

and the stability limit can be represented by

$$U_{rr}^{(r-1)} = \Delta_{r} = \det | \underline{U} | = 0.$$
 (3.43)

The condition for the stability limit expressed as $\Delta_r = 0$ is in the final form as given by Gibbs and is in the form used for computation by Heidemann and Khalil. Equivalent forms are obtained when working with a Legendre transformation of the energy representation. In general, the stability limit can be expressed

$$\begin{bmatrix} U^{i} \end{bmatrix}_{(r-i)(r-i)}^{(r-i-1)} = \Delta_{r-i} = 0.$$
(3.44)

Before moving on to a discussion of the cubic form, there is one final point to be made regarding the quadratic form which is suggested by the condition for the limit of stability written as a determinant. Consider the energy formulation. At the stability limit, eq. (3.43) implies that \underline{V} is a singular matrix. We have mentioned previously that \underline{V} represents a transformation between the extensive and intensive system variables. When a sys-

tem is in a regular state (i.e., \underline{V} is not singular) then a set of r extensive variables uniquely specifies a set of r intensive variables (recall that x_{r+1} has been fixed to specify the size of the system). This is in accord with Gibbs' phase rule, i.e., the number of independent intensive variables in a single phase system is c+1 = r. At the limit of stability, the rank of \underline{V} is reduced from r to r-1; hence, there are only r-1 independent intensive variables. Since \underline{V} is singular, there exists a non-trivial solution to the homogeneous equation

$$\underbrace{U}_{Z} = \underbrace{O}_{A} . \tag{3.45}$$

Thus, the virtual process which causes the quadratic form to be zero at the stability limit defines a unique direction in Gibbs space within an arbitrary sign; this process is referred to as a critical displacement. Furthermore, the critical displacement expressed by eq (3.45) represents a virtual process in which the r-1 independent intensities are held constant (recall eq (3.17)).

3.2 The Cubic Form

The condition $\delta^3 U = 0$ is necessary, but not sufficient, to prove the stability of a system on the stability limit. In this section two formulations of the condition $\delta^3 U = 0$ will be presented. Analogous formulations in terms of the Legendre transforms simply involve fewer independent variables.

The previous section established that, for a system on the stability limit, there exists a virtual process, unique within an arbitrary multiplicative constant, called the critical displacement for which the quadratic form becomes identically zero. Therefore, the critical displacement is the only process which needs to be considered when evaluating the cubic form.

The cubic form is a special case of a general tri-linear form. Its linearity allows it (2.10) to be written as

$$\delta^{3} U = \sum_{k=1}^{r} Z_{k} \frac{\partial}{\partial X_{k}} \begin{bmatrix} r & \frac{\partial^{2} U}{\partial X_{i} \partial X_{j}} \\ i, j=1 \end{bmatrix} Z_{i} Z_{j}^{2}$$
(3.46)

or

$$\delta^{3} U = \sum_{k=1}^{r} Z_{k} \frac{\partial}{\partial X_{k}} [\delta^{2} U], \qquad (3.47)$$

or

$$\delta^{3} U = \underline{Z} \cdot \nabla \left(\delta^{2} U \right), \qquad (3.48)$$

where ∇ is a gradient operator with components $\frac{\partial}{\partial X_i}$. The operator $\underline{Z} \cdot \nabla$ produces a directional derivative, that is, the derivative in the direction of the vector \underline{Z} in Gibbs space. (Gibbs space is taken here to be spanned by the variables S, V, n_1 , ..., n_{c-1} .) Hence, eq (3.48) indicates that the cubic form necessary to show the stability of a system on the stability limit is the derivative of the quadratic form in the direction of the critical displacement. To evaluate the cubic form, the direction of the critical displacement vector must be known; this vector is determined for systems on the stability limit by solving eq (3.45).

Gibbs formulated the second condition for a critical point in a way which avoided having to explicitly determine the critical displacement vector. His formulation is more general than is the specification that $\delta^3 U = 0$, but it contains a redundancy which is extremely costly from a computational point of view. To formulate Gibbs' second condition we proceed as follows.

The critical displacement is one in which r-1 of the r intensities are held constant. To consider virtual processes of this type, choose any r-1 of the r equations represented by eq (3.45) to act as constraints on the r independent extensive variations Z_i , i = 1, ..., r. For definiteness choose the first r-1 equations. These equations impose the constraint that the r-1 intensities $\frac{\partial U}{\partial X_i}$, i = 1, ..., r-1, are constant in any virtual process. The only independent variation is δX_r which may be chosen to be arbitrarily small as required to determine local stability. For the final equation consider an analog to the cubic form; that is, rather than take a directional derivative of the quadratic form, differentiate the discriminant Δ_r which is an equivalent indicator of the stability limit. Just as $\underline{Z} \cdot \nabla(\delta^2 U)$ must be zero for a critical point, so must $Z \cdot \nabla(\Delta_r)$. Then our final set of equations is

$$\begin{bmatrix} U_{11} & U_{12} & \cdots & U_{1r} \\ \vdots & \vdots & & \vdots \\ U_{r-1,1} & U_{r-1,2} & \cdots & U_{r-1,r} \\ \frac{\partial \Delta_r}{\partial x_1} & \frac{\partial \Delta_r}{\partial x_2} & \cdots & \frac{\partial \Delta_r}{\partial x_r} \end{bmatrix} \begin{bmatrix} \delta X_1 \\ \vdots \\ \delta X_{r-1} \\ \delta X_r \end{bmatrix} = \underline{0} .$$
(3.49)

A nontrivial solution to eq (3.49) requires the matrix to have a zero determinant, which is Gibbs' second condition for a critical point.

3.3 Computational Considerations

Let us first consider the computations required by Gibbs' formulation for a critical point. The conditions are that $\Delta_r = 0$ (eq (3.43)) and that $\Delta_r^{\dagger} = 0$, where Δ_r^{\dagger} is the determinant of the matrix in eq (3.49). Both conditions involve r^{th} order determinants, however, the second condition contains derivatives of Δ_r within the determinant Δ_r^{\dagger} . An exact formula for the derivative of a determinant is derived by expressing the determinant as a multiple matrix U, then (Courant and John [1])

$$\Delta_{\mathbf{r}} = \det \left| \underbrace{\mathbf{U}}_{\underline{\mathbf{v}}} \right| = \underbrace{\mathbf{U}}_{1} \times \underbrace{\mathbf{U}}_{2} \times \cdots \times \underbrace{\mathbf{U}}_{\mathbf{r}-1} \cdot \underbrace{\mathbf{U}}_{\mathbf{r}}$$
(3.50)

where x is a vector cross product and • is a vector dot product. Differentiating (3.50) gives

$$\frac{\partial \Delta_{\mathbf{r}}}{\partial \mathbf{X}_{\mathbf{i}}} = \frac{\partial \underline{U}_{1}}{\partial \mathbf{X}_{\mathbf{i}}} \times \underline{U}_{2} \times \cdots \times \underline{U}_{\mathbf{r}-1} \cdot \underline{U}_{\mathbf{r}}$$

$$+ \underline{U}_{1} \times \frac{\partial \underline{U}_{2}}{\partial \mathbf{X}_{\mathbf{i}}} \times \cdots \times \underline{U}_{\mathbf{r}-1} \cdot \underline{U}_{\mathbf{r}} \qquad (3.51)$$

$$+ \cdots$$

$$+ \underline{U}_{1} \times \underline{U}_{2} \times \cdots \times \underline{U}_{\mathbf{r}-1} \cdot \frac{\partial \underline{U}_{\mathbf{r}}}{\partial \mathbf{X}_{\mathbf{i}}};$$

hence, the derivative of an r^{th} order determinant equals the sum of r determinants, in each of which one column is replaced by its derivative with respect to the appropriate independent variable. Hence, to evaluate Gibbs' conditions for a critical point of a single state requires the evaluation of $(r^2 + 2) r^{th}$ order determinants. The most efficient way to compute a determinant is to factor the matrix and then compute the product of the pivots. Matrix factorization requires approximately $r^3/3$ operations; therefore, the computational effort required to evaluate Gibbs' conditions is proportional to r^5 .

The efficiency of the method proposed by Heidemann and Khalil for computing critical points comes from their realization that if eq (3.45) is solved for the critical displacement vector \underline{Z} , then the cubic form may be evaluated directly. Direct evaluation of the cubic form requires r^3 operations. It will be shown later that for some equations of state, such as the general two-constant cubic equation to be considered, the cubic form can be analytically summed in such a way as to reduce the computational effort required for its evaluation to being proportional to r^2 . When the cubic form may be simplified in that way, the major portion of the critical point calculation is required to factor the matrix \underline{V} ; thus the overall effort remains proportional to r^3 .

In addition to the difference in computational effort required by the two formulations presented above, they require distinct iteration schemes which will be discussed here. The conditions of criticality will be expressed in terms of the Helmholtz free energy, and the set of independent variables is taken as (T, V, n_1 , ..., n_{c-1}). Since there are two conditions of criticality, we will specify the composition of the mixture of interest and then solve two equations for the values of T, V at a critical point. Critical pressure is subsequently obtained from the equation of state.

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Gibbs' formulation results in the equations

$$\Delta_{r-1} = 0 , \quad \Delta_{r-1}' = 0 . \quad (3.52)$$

These equations may be solved using a Newton-Raphson iteration scheme. The derivatives of the determinants required for the iteration are normally computed numerically. Equation (3.52) may be evaluated at any state point, and the critical point results will be correct as long as the stability limit is approached from a stable region.

Heidemann and Khalil formulated the critical point as

$$\Delta_{r-1} = 0 , \quad \delta^3 A = 0 . \quad (3.53)$$

The solution procedure must be modified from a straightfoward Newton-Raphson technique because the cubic form can be evaluated only at a state on the stability limit. Therefore, if the volume is specified, the temperature on the stability limit may be determined by solving $\Delta_{r-1} = 0$ using a one-dimensional Newton-Raphson iteration. Then the critical displacement vector is determined by solving $\underline{A} \ \underline{Z} = \underline{0}$, and the cubic form is evaluated. The search has now been reduced to a one-dimensional search for the critical point along the limit of stability. The derivative of the cubic form with respect to volume along the stability limit is determined numerically, and a Newton-Raphson iteration employed to update the volume. This procedure of nested one-dimensional searches is continued until a critical point is found. In addition to the efficiency of computing $\delta^3 A$ rather than Δ_{r-1}^{i} , the formulation of Heidemann and Khalil appears to have a larger radius of convergence. Heidemann and Khalil reported that a single strategy for the initial guess was sufficient to compute critical points for the large group of mixtures they considered.

4. The Method of Heidemann and Khalil

Heidemann and Khalil chose to work with the stability conditions written in terms of the Helmholtz free energy; this is the logical choice when working with equations of state with T, V, n_1 , ..., n_c as the independent variables. Thus, all virtual processes are carried out at constant temperature. Furthermore, Heidemann and Khalil fixed the size of the system by arbitrarily holding V constant, rather than N as was done in the theory sections of this note; this results in the independent variable set n_1 , n_2 , ..., n_c , where c is the number of components in the mixture. Their claim that this choice of variables "has the effect of producing symmetrical quadratic and cubic forms" is misleading. The symmetry of the quadratic and cubic forms is predicated on the order of differentiation in the second and third order derivatives of the free energy being arbitrary. In general, the variables n_1 , n_2 , ..., n_c are convenient from the point of view of computations because all the derivatives of the free energy will have the same form. Furthermore, for the particular equation of state to be examined in this work, this choice of variables results in significant simplifications in the analytical expressions of the quadratic and cubic forms.

In terms of the Helmholtz free energy (A), the stability limit is expressed by the condition (dropping the subscript on $\Delta_{r=1}$)

$$\Delta \equiv \det \left[\mathbf{Q} \right] = 0 \tag{4.1}$$

where the components of the c x c matrix Q are

$$q_{ij} = \frac{\partial^2 A}{\partial n_i \partial n_j} .$$
 (4.2)

For a specified value of V, eq (4.1) is used to determine the value of T on the stability limit. Because of the expense of computing $\frac{\partial \Delta}{\partial T}$ analytically, and because the computation of Δ itself is the most time consuming part of the critical point computation, a quasi-Newton iteration is used to solve (4.1). This technique involves computing $\frac{\partial \Delta}{\partial T}$ numerically on the first iteration, i.e.,

$$\frac{\partial \Delta(T_{o})}{\partial T} = \frac{\Delta(T_{o} + \delta T) - \Delta(T_{o})}{\delta T}, \qquad (4.3)$$

where $\delta T = 10^{-8} T_0$, T_0 is the initial temperature guess, and $\Delta(T)$ indicates the determinant evaluated at T (V, n₁, ..., n_c are fixed during the temperature iteration). On subsequent iterations use

$$\frac{\partial \Delta(T_i)}{\partial T} = \frac{\Delta(T_i) - \Delta(T_{i-1})}{T_i - T_{i-1}}$$
(4.4)

where T_i is the temperature after the ith iteration which is obtained from

$$T_{i+1} = T_i - \frac{\Delta(T_i)}{\frac{\partial\Delta(T_i)}{\frac{\partial}{\partial T}}} .$$
(4.5)

The quasi-Newton iteration exhibits superlinear convergence, and requires only one evaluation of Δ per iteration (after the first). The determinant computation is performed by subroutines DSPFA and DSPDI from the LINPACK software (Dongarra et al. [2]). The first routine factors a symmetric indefinite matrix (stored in packed form) and the second computes the determinant as a product of the pivots.

Once the iteration to find the stability limit has converged, the cubic form is evaluated: the first step in this process is to determine the critical displacement vector \underline{Z} ; i.e., solve

In general this step is efficiently performed by the inverse iteration technique (Peters and Wilkinson [11]). In the implementation described here, \underline{Z} is obtained from the LINPACK subroutine DSPCO.

Because \underline{Z} is determined only within an arbitrary multiplicative constant, it must be subjected to further constraints to avoid arbitrary changes in the sign or magnitude of the cubic form evaluated along the stability limit; such changes falsely indicate the location of critical points. The "length" of \underline{Z} is normalized by the constraint

$$\underline{Z}^{\mathrm{T}} \underline{Z} = 1 \quad . \tag{4.7}$$

We determine the direction of \underline{Z} by specifying that its first component δn_1 be positive at the initial guess of the volume. Constraining δn_1 to be positive to fix the direction of \underline{Z} cannot be continued as we move along the stability limit searching for the zero of the cubic form. Because it is possible for δn_1 to go through a zero as \underline{Z} changes with V along the stability limit, constraining δn_1 to always be positive would be equivalent to changing the direction of \underline{Z} at a value of the volume where δn_1 goes through a zero. The technique used to ensure that the direction of \underline{Z} varies continuously as a function of V along the stability limit is the following. The null vector from the previous iteration on V is saved and projected onto the null vector computed for the current iteration. If the projection is positive we assume that the direction of Z is changing continuously. This final condition on Z may be written

$$\underline{Z}_{i-1}^{T} \quad \underline{Z}_{i} > 0 , \qquad (4.8)$$

where \underline{Z}_i is the null vector from the ith iteration on V. If \underline{Z}_i does not satisfy (4.8), it is multiplied by -1 so that it does.

Michelsen and Heidemann [7] have recommended that discontinuities in \underline{Z} be avoided by making use of the condition

$$\underline{z}_{0}^{T} \underline{z}_{i} > 0$$
 , (4.9)

where \underline{Z}_{0} corresponds to the initial guess V_{0} . Depending on how far V_{0} is from the critical point, it is quite possible that \underline{Z} could change enough along the stability limit that eq (4.9) would result in an arbitrary change in direction. It seems safer, and no more costly, to employ eq (4.8).

The summation of the cubic form can in general be reduced from c^3 terms to c(c+1)(c+2)/6 by making use of its symmetry properties, i.e.,

$$\delta^{3}A = \sum_{i,j,k=1}^{C} A_{ijk} Z_{i}Z_{j}Z_{k} = \sum_{k=j}^{C} \sum_{j=i}^{C} \sum_{i=1}^{C} h_{ijk} A_{ijk} Z_{i}Z_{j}Z_{k}$$
(4.10)

where

For the special case of the two-constant cubic equation of state to be considered here, the cubic form has been simplified so that only a double summation is required for its evaluation.

Michelsen [6] suggested that the cubic form could be evaluated numerically because it is the derivative of the quadratic form in the direction of the critical displacement vector; hence,

$$\delta^{3} A = C = \frac{\underline{Z}^{T} \underline{Q}(T, V, \underline{n} + \underline{\varepsilon} \underline{Z}) \underline{Z} - \underline{Z}^{T} \underline{Q}(T, V, \underline{n}) \underline{Z}}{\|\underline{\varepsilon} \underline{Z}\|}$$
(4.11)

where

<u>n</u> is a vector of the mole numbers, i.e., $(n_1, n_2, ..., n_c)^T$, ε is a small number, i.e., $O(10^{-6})$, $\underline{Z}^T \underline{Q}(T, V, \underline{n})\underline{Z} = 0$ on stability limit, $\|\varepsilon\underline{Z}\| = \varepsilon \|\underline{Z}\| = \varepsilon$, since $\|\underline{Z}\| \equiv \underline{Z}^T\underline{Z} = 1$. This expression for the cubic form is particularly useful when the required derivatives of A are not expressible analytically.

Once the stability limit is located and the cubic form is evaluated at the current value, $\text{V}_{\rm i},$ the volume is updated by

$$V_{i+1} = V_i - \frac{C(V_i)}{C'(V_i)}$$
, (4.12)

where C'(V_i) represents the derivative of C with respect to the volume (dC/dV) or some estimate of it. The original method of Heidemann and Khalil approximated dC/dV numerically, i.e.,

$$\frac{d C(V_i)}{dV} = \frac{C (V_i + \delta V) - C (V_i)}{\delta V}$$
(4.13)

where $\delta V = 10^{-5}V_i$. This approximation is expensive because, when the volume is incremented, eqs (4.1) and (4.6) must be solved again before evaluating $C(V_i + \delta V)$. A good approximation can be made for $T(V_i + \delta V)$ with only an inexpensive calculation (see below) so that only one or two iterations are required to solve (4.1). But we must keep in mind that the single most expensive calculation in this method is the factorization of Q; thus we should try to minimize the number of evaluations of the cubic form. Michelsen and Heidemann [7] presented a quasi-Newton method which requires only a single evaluation of C for each iteration on V. In general, they used

$$C'(V_{i}) = \frac{C(V_{i}) - C(V_{i-1})}{V_{i} - V_{i-1}} .$$
(4.14)

Two values of C are needed to start this iteration. One option is to use (4.13) for the first iteration, then switch to (4.14) for subsequent iterations. Michelsen and Heidemann chose to use a modified form of (4.13) for the first iteration. To evaluate $C(V_i + \delta V)$ they make two approximations: first, that $\underline{Z}_1 = \underline{Z}_0$, and second, that T ($V_i + \delta V$) is obtained from a Taylor series expansion, i.e.,

$$T(V_{i} + \delta V) = T(V_{i}) + \delta V \frac{dT}{dV} |_{V_{i}}, \qquad (4.15)$$

where $T(V_i + \delta V)$ is the first order approximation to the temperature on the stability limit at $(V_i + \delta V)$, $T(V_i)$ is the temperature on the stability limit at V_i , and dT/dV is the derivative along the stability limit. To obtain an expression for this derivative, consider the stability limit for a given mixture (fix <u>n</u>) to be parameterized in terms of V. Since the stability limit is defined by $\underline{Z}^T\underline{Q} \ \underline{Z} = 0$, then

$$\frac{d}{dV} \left(\underline{Z}^{T} \underline{Q} \ \underline{Z} \right) = \frac{d\underline{Z}^{T}}{dV} \ \underline{Q} \ \underline{Z} + \underline{Z}^{T} \ \frac{d\underline{Q}}{dV} \ \underline{Z} + \underline{Z}^{T} \underline{Q} \ \frac{d\underline{Z}}{dV} = 0$$

$$= \underline{Z}^{T} \ \frac{d\underline{Q}}{dV} \ \underline{Z} = 0$$

$$(4.16)$$

Since $Q Z = Z^T Q = 0$. By chain rule,

$$\frac{\mathrm{d}\mathbb{Q}}{\mathrm{d}\mathbb{V}} = \frac{\partial\mathbb{Q}}{\partial\mathbb{V}} + \frac{\partial\mathbb{Q}}{\partial\mathrm{T}}\frac{\mathrm{d}\mathrm{T}}{\mathrm{d}\mathbb{V}} \quad . \tag{4.17}$$

Substitution of (4.17) into (4.16) gives

$$\frac{\mathrm{dT}}{\mathrm{dV}} = -\frac{Z}{\frac{Z}{2}} \frac{\overline{\partial V}}{\overline{\partial V}} \frac{Z}{Z}}{\frac{Z}{2}} . \qquad (4.18)$$

These two approximations allow an estimate of $C(V_i + \delta V)$ which requires no additional factorizations of Q. After the initial iteration on V, $C(V_i)$ in (4.14) is evaluated exactly, and the initial guess of temperature at a new volume V_i is made analogously to (4.15), i.e.,

$$T_{O}(V_{i}) = T(V_{i-1}) + (V_{i} - V_{i-1}) \frac{dT}{dV} \Big|_{V_{i-1}} .$$
 (4.19)

Although the quasi-Newton method requires only half the number of evaluations of the cubic form per iteration on V as does the full Newton-Raphson technique described initially, its convergence is slower (superlinear rather than quadratic). In general, the cost of computing critical points by various methods will depend on the cost of computing the derivative $C'(V_i)$ relative to the convergence rate which can be attained with that approximation. This must be determined by numerical experiments.

4.1 Analytical Expression for the Volume Derivative of the Cubic Form

It may be advantageous to retain the quadratic convergence of a Newton-Raphson iteration if the derivative of the cubic form with respect to volume can be computed more efficiently. In this section is presented an analytical derivation of dC/dV which requires one additional factorization of an augmented \underline{Q} matrix to be computed for each volume iteration. The

procedure is substantially more efficient than the forward difference approximation of dC/dV (eq 4.13) which requires two evaluations of C at each volume iteration.

We begin, as previously for dT/dV, by considering the stability limit to be parameterized in terms of V. Then

$$\frac{\mathrm{dC}}{\mathrm{dV}} = \sum_{i,j,k=1}^{C} \left[\frac{\mathrm{dA}_{ijk}}{\mathrm{dV}} \quad z_{i}z_{j}z_{k} + 3A_{ijk} - \frac{\mathrm{dZ}_{i}}{\mathrm{dV}} \quad z_{j}z_{k} \right]$$
(4.20)

where

$$\frac{dA}{dV} = \frac{\partial A}{\partial V} + \frac{\partial A}{\partial T} \frac{dT}{dV}$$
(4.21)

The partials ($\partial A_{ijk}/\partial V$) and ($\partial A_{ijk}/\partial T$) may be obtained by differentiation of the expression

for A_{ijk} obtained from the equation of state. The derivative $\frac{dZ}{dV}$ is obtained from the following considerations. Differentiating the expression Q Z, which is zero on the stability limit, leads to

$$Q = \frac{dZ}{dV} = -\frac{dQ}{dV} \frac{Z}{Z} . \qquad (4.22)$$

This expression could be solved for $\frac{dZ}{dV}$ except that Q is singular on the stability limit.

Therefore we must find another condition on $\frac{dZ}{dV}$ which will be used to replace the row in Q containing the zero pivot. The appropriate condition is from a simple result of vector calculus: the derivative of a vector of constant length is orthogonal to that vector, i.e.,

$$\underline{Z}^{\mathrm{T}} \frac{\mathrm{d}\underline{Z}}{\mathrm{d}V} = 0 \quad . \tag{4.23}$$

This condition can be combined with (4.22) and the result written as the solution of c+1 equations in c unknowns,

$$\begin{bmatrix} \underline{Q} \\ -\underline{Z} \\ -\underline{Z} \end{bmatrix} \begin{bmatrix} \underline{dZ} \\ \underline{dV} \end{bmatrix} = \begin{bmatrix} \underline{dQ} \\ -\underline{dV} \\ -\underline{Z} \\ -\underline{O} \end{bmatrix} . \qquad (4.24)$$

5. Implementation for a Two-Constant Cubic Equation of State

Expressions for the derivatives of the Helmholtz free energy are required to evaluate Δ , C, and their derivatives with respect to T and V. These expressions are given here for a general two-constant cubic equation of state (TCC EOS) following, for the most part, the notation of Michelson and Heidemann [7].

The TCC EOS is written

$$P = \frac{NRT}{V-Nb} - \frac{N^2 a}{(V + \delta_1 Nb)(V + \delta_2 Nb)}, \qquad (5.1)$$

where

$$a = \frac{1}{N^{2}} \sum_{i,j=1}^{C} n_{i}n_{j}a_{ij}, \qquad (5.2)$$

$$b = \frac{1}{N} \sum_{i=1}^{C} n_i b_i$$
, (5.3)

$$N = \sum_{i=1}^{C} n_i$$

,

$$a_{ij} = \xi_{ij} (a_{ii} a_{jj})^{1/2}$$
, (5.4)

$$a_{ii} = \Omega_a R^2 T_{ci}^2 / P_{ci} \{1 + m_i [1 - (T/T_{ci})^{1/2}]\}^2, \qquad (5.5)$$

 $m_i = m(\omega_i)$,

$$b_i = \Omega_b RT_{ci}/P_{ci} .$$
 (5.6)

For the SRK equation of state,

$$\delta_1 = 1, \ \delta_2 = 0, \ \Omega_a = 0.42748, \ \Omega_b = 0.08664$$
, (5.7)

$$m(\omega_i) = 0.480 + 1.574\omega_i - 0.176\omega_i^2$$
, (5.8)

and for the PR equation of state,

$$\delta_1 = 1 + \sqrt{2}, \ \delta_2 = 1 - \sqrt{2}, \ \Omega_a = 0.45724, \ \Omega_b = 0.07780$$
, (5.9)

$$m(\omega_i) = 0.37464 + 1.54226 \omega_i - 0.26992 \omega_i^2$$
 (5.10)

Heidemann and Khalil chose to proceed from the expression for fugacity

$$\operatorname{RT} \ln f_{i} = -\int_{\infty}^{V} \left[\frac{\partial P}{\partial n_{i}}\right]_{T, V, n_{j}} - \frac{\operatorname{RT}}{V} dV + \operatorname{RT} \ln \frac{n_{i} \operatorname{RT}}{V} . \qquad (5.11)$$

Their choice of $(n_1, n_2, ..., n_c)$ as the independent variables results in all derivatives containing differentiations with respect to a mole number. However, if one of the mole numbers in the independent variable set were to be replaced with the volume, then one element of $\frac{Q}{2}$ (i.e., $\frac{\partial^2 A}{\partial v^2}$) would contain no differentiations with respect to mole number. In that case, those derivatives would have to obtained by differentiating the Helmholtz free energy rather than the fugacity. To be consistent with any derivatives obtained from the fugacity, the free energy must be relative to a reference state of pure ideal gases at the system temperature and unit pressure, i.e. (see Prausnitz [12], p. 40),

$$A - A^{O} = -\int_{\infty}^{V} (P - \frac{NRT}{V}) dV - RT \sum_{i=1}^{C} n_{i} \ln \frac{V}{n_{i}RT}, \qquad (5.12)$$

where

$$A^{\circ} \cong \sum_{i=1}^{C} A_{i}^{\circ}$$
.

 A_i^0 = Helmholtz free energy of pure i in an ideal gas state at the system T, and p = 1. When this expression is differentiated with respect to mole numbers,

$$\frac{\partial A_{i}^{O}}{\partial n_{i}} \middle|_{T,V} = \mu_{i}^{O} - RT , \qquad (5.13)$$

where μ_{i}^{O} = the chemical potential of pure i in an ideal gas state at the system T, and p = 1.

The Helmholtz free energy for the TCC EOS is

$$A - A^{\circ} = RT \sum_{i=1}^{c} n_{i} \ln \frac{n_{i}RTF_{1}}{Nb} - \frac{Na}{2b}F_{5}$$
, (5.14)

where F_i are functions of the dimensionless volume K (= V/Nb) which are summarized at the end of this section. Differentiating (5.14) with respect to mole numbers gives

RT ln
$$f_i = RT \left(ln \frac{n_i RTF_1}{Nb} + \beta_i F_1 \right) - \frac{a}{b} \left(\alpha_i F_5 + \frac{\beta_i}{2} F_6 \right)$$
, (5.15)

where

$$\alpha_{i} = \frac{1}{a} \sum_{j=1}^{C} \frac{n_{j} a_{ij}}{N} , \qquad (5.16)$$

$$\beta_{i} = \frac{b_{i}}{b}$$

The elements of \mathbb{Q} are obtained from further differentiation of (5.15) with respect to mole numbers, i.e.,

$$Nq_{ij} = NRT \left(\frac{\partial \ln f_{i}}{\partial n_{j}}\right)_{T,V,n_{k}} = RT \left[\frac{N \delta_{ij}}{n_{i}} + (\beta_{i} + \beta_{j}) F_{1} + \beta_{i}\beta_{j} F_{1}^{2}\right]$$

$$+ \frac{a}{b} \left[\beta_{i}\beta_{j}F_{3} - (\frac{a_{ij}}{a}) F_{5} + (\beta_{i}\beta_{j} - \alpha_{i}\beta_{j} - \alpha_{j}\beta_{i})F_{6}\right],$$
(5.18)

where δ_{ij} is the Kronecker delta, and n_k held constant in the differentiation signifies that all mole numbers are held constant except n_j .

To evaluate the cubic form one further differentiation of (5.18) with respect to the mole numbers is required, i.e.,

$$N^{2}A_{ijk} = N^{2} RT \left(\frac{\partial^{2} \ln f_{i}}{\partial n_{j} \partial n_{k}}\right)_{T,V, n_{k}}$$

$$= RT \left[-\frac{N^{2} \delta_{ij} \delta_{ik}}{n_{i}^{2}} + (\beta_{i}\beta_{j} + \beta_{i}\beta_{k} + \beta_{j}\beta_{k})F_{1}^{2} + 2\beta_{i}\beta_{j}\beta_{k} F_{1}^{3}\right]$$

$$+ \frac{a}{b} \left\{ \left[2 (\alpha_{i}\beta_{j}\beta_{k} + \alpha_{j}\beta_{i}\beta_{k} + \alpha_{k}\beta_{i}\beta_{j}) - 3\beta_{i}\beta_{j}\beta_{k}\right](F_{3} + F_{6}) - 2\beta_{i}\beta_{j}\beta_{k} F_{4} - \frac{1}{a} (a_{ij}\beta_{k} + a_{ik}\beta_{j} + a_{jk}\beta_{i})F_{6} \right\},$$
(5.19)

When this expression is substituted into the cubic form, algebraic simplification yields

$$N^{2}RT \sum_{i,j,k=1}^{c} \frac{\partial^{2} \ln f_{i}}{\partial n_{j} \partial n_{k}} Z_{i}Z_{j}Z_{k} = RT \left[-\sum_{i=1}^{c} \frac{N^{2} Z_{i}^{3}}{n_{i}^{2}} + 3 \overline{Z} (\overline{\beta} F_{1})^{2} + 2(\overline{\beta} F_{1})^{3} \right]$$
(5.20)

$$+\frac{a}{b}\left[(6\overline{\alpha}\ \overline{\beta}^2 - 3\overline{\beta}^3)(F_3 + F_6) - 2\overline{\beta}^3F_4 - 3\ \overline{a}\ \overline{\beta}\ F_6\right],$$

where

$$\overline{Z} = \sum_{i}^{\infty} Z_{i}, \qquad (5.21)$$

$$\overline{\alpha} \equiv \sum_{i} \alpha_{i} Z_{i} , \qquad (5.22)$$

$$\overline{\beta} \equiv \sum_{i} \beta_{i} Z_{i} , \qquad (5.23)$$

$$\overline{a} = \frac{1}{a} \sum_{i j} a_{ij} Z_{i} Z_{j} .$$
(5.24)

(There is a typographic error in the last term on the right side of eq (18) in the paper by Michelsen and Heidemann [7].) To compute dT/dV along the stability limit, we need the partial derivatives of $q_{i,j}$ with respect to T and V; these are given by

$$N \frac{\partial}{\partial K} q_{ij} = RT \left[(\beta_i + \beta_j) \frac{\partial F_1}{\partial K} + 2 \beta_i \beta_j F_1 \frac{\partial F_1}{\partial K} \right]$$

$$+ \frac{a}{b} \left[\beta_i \beta_j \frac{\partial F_3}{\partial K} - \frac{a_{ij}}{a} \frac{\partial F_5}{\partial K} + (\beta_i \beta_j - \alpha_i \beta_j - \alpha_j \beta_i) \frac{\partial F_6}{\partial K} \right],$$
(5.25)

where the derivatives of the ${\rm F}_{\rm i}$ with respect to the dimensionless volume K are given at the end of this section, and

$$N \frac{\partial}{\partial T} q_{ij} = R \left[\frac{N \delta_{ij}}{n_i} + (\beta_i + \beta_j) F_1 + \beta_i \beta_j F_1^2 \right] + \frac{\partial a}{\partial T} \frac{\beta_i \beta_j}{b} (F_3 + F_6)$$

$$- \frac{\partial}{\partial T} \frac{a_{ij}}{b} \frac{F_5}{b} - \left[\frac{\partial(a\alpha_i)}{\partial T} \frac{\beta_j}{b} + \frac{\partial(a\alpha_j)}{\partial T} \frac{\beta_i}{b} \right] F_6 ,$$
(5.26)

where

$$\frac{\partial a_{ii}}{\partial T} = \Omega_a \frac{(R T_{ci})^2}{P_{ci}^2} \left\{ 1 + m_i \left[1 - \left(\frac{T}{T_{ci}}\right)^{1/2} \right] \right\} \left[\frac{-m_i}{(T T_{ci})^{1/2}} \right]$$
(5.27)

$$\frac{\partial a_{ij}}{\partial T} = \frac{1/2 \xi_{ij}}{(a_{ii}a_{jj})^{1/2}} \left(\frac{\partial a_{ii}}{\partial T} a_{jj} + a_{ii} \frac{\partial a_{jj}}{\partial T} \right)$$
(5.28)

$$\frac{\partial (a\alpha_{i})}{\partial T} = \frac{1}{N} \sum_{j=1}^{C} n_{j} \frac{\partial a_{ij}}{\partial T}$$
(5.29)

$$\frac{\partial a}{\partial T} = \frac{1}{N^2} \sum_{i,j=1}^{C} n_i n_j \frac{\partial a_{ij}}{\partial T} .$$
(5.30)

The quadratic forms required to evaluate dT/dV can be simplified to:

$$N \underline{Z}^{T} \frac{\partial \underline{Q}}{\partial K} \underline{Z} = RT (2 \overline{\beta} \overline{Z} F_{K1} + 2 \overline{\beta}^{2} F_{1} F_{K1})$$

$$+ \frac{a}{b} [\overline{\beta}^{2} F_{K3} - \overline{a} F_{K5} + (\overline{\beta}^{2} - 2 \overline{\alpha} \overline{\beta}) F_{K6}]$$
(5.31)

and

$$N \underline{Z}^{T} \frac{\partial \underline{Q}}{\partial T} \underline{Z} = R \left(N \sum_{i} \frac{z_{i}^{2}}{n_{i}} + 2 \overline{\beta} \overline{Z} F_{1} + \overline{\beta}^{2} F_{1}^{2} \right)$$

$$+ \frac{1}{b} \left[a_{T} \overline{\beta}^{2} (F_{3} + F_{6}) - \overline{a}_{T} F_{5} - 2 \overline{\alpha}_{T} \overline{\beta} F_{6} \right],$$
(5.32)

where

$$F_{ki} \equiv \frac{\partial F_i}{\partial K} , \qquad (5.33)$$

$$a_{T} = \frac{\partial a}{\partial T}$$
, (5.34)

$$\overline{\alpha}_{\mathrm{T}} = \sum_{i=1}^{c} \frac{\partial(a\alpha_{i})}{\partial \mathrm{T}} Z_{i} , \qquad (5.35)$$

$$\overline{a}_{T} = \sum_{i,j=1}^{c} \frac{\partial a_{ij}}{\partial T} Z_{i}Z_{j} .$$
(5.36)

Dividing (5.31) by (5.32) gives dT/dK on the stability limit which is different from dT/dV by a factor of Nb.

To obtain the derivative of the cubic form with respect to K along the stability limit, differentiating C (5.20) directly gives

$$N^{2} \frac{dC}{dK} = RT_{K} \left[-\sum_{i=1}^{c} \frac{N^{2} z_{i}^{3}}{n_{i}^{2}} + 3 \bar{z} (\bar{\beta} F_{1})^{2} + 2 (\bar{\beta} F_{1})^{3} \right]$$

+ $3RT \left[-\sum_{i=1}^{c} \frac{N^{2} z_{i}^{2} z_{Ki}}{n_{i}^{2}} + (\bar{z}_{K}\bar{\beta}^{2} + 2\bar{z}\bar{\beta} \bar{\beta}_{K})F_{1}^{2} + 2\bar{z}\bar{\beta}^{2} F_{1}F_{K1} \right]$
+ $2 \bar{\beta}^{2} \bar{\beta}_{K} F_{1}^{3} + 2\bar{\beta}^{3} F_{1}^{2} F_{K1} \right]$
+ $\frac{1}{b} \left\{ (6 a\bar{\alpha}\bar{\beta}^{2} - 3a\bar{\beta}^{3})(F_{K3} + F_{K6}) + [6((a\bar{\alpha})_{K} \bar{\beta}^{2} + 2 a\bar{\alpha}\bar{\beta}\bar{\beta}_{K}) \right\}$ (5.37)

$$-3 (a_{K}\bar{\beta}^{3} + 3a\bar{\beta}^{2}\bar{\beta}_{K})] (F_{3} + F_{6})$$

$$-2 [(a_{K}\bar{\beta}^{3} + 3a\bar{\beta}^{2}\bar{\beta}_{K})F_{4} + a\bar{\beta}^{3}F_{K4}]$$

$$-3 [((a\bar{a})_{K}\bar{\beta} + a\bar{a}\bar{\beta}_{K})F_{6} + a\bar{a}\bar{\beta}F_{K6}]],$$

where

$$I_{\rm K} = \frac{{\rm d}T}{{\rm d}K} , \qquad (5.38)$$

$$Z_{Ki} \equiv \frac{dZ_i}{dK} = i^{th} \text{ component of } \frac{dZ}{dK},$$
 (5.39)

$$\bar{Z}_{K} \equiv \frac{d\bar{Z}}{dK} = \sum_{i=1}^{C} Z_{Ki} , \qquad (5.40)$$

$$\hat{\beta}_{K} \equiv \frac{d\hat{\beta}}{dK} = \sum_{i=1}^{C} \beta_{i} Z_{Ki} , \qquad (5.41)$$

$$a_{K} \equiv \frac{da}{dK} = \frac{\partial a}{\partial T} \frac{dT}{dK} , \qquad (5.42)$$

$$(a\overline{\alpha})_{K} \equiv \frac{d(a\overline{\alpha})}{dK} = \sum_{i=1}^{C} (a\alpha_{i} Z_{Ki} + Z_{i} \frac{d(a\alpha_{i})}{dK}), \qquad (5.43)$$

$$\frac{d(a\alpha_i)}{dK} = \frac{\partial(a\alpha_i)}{\partial T} \frac{dT}{dK} , \qquad (5.44)$$

$$(a\bar{a})_{K} \equiv \frac{d(a\bar{a})}{dK} = \sum_{i,j=1}^{C} (Z_{Ki} Z_{j} a_{ij} + Z_{i} Z_{Kj} a_{ij} + Z_{i} Z_{j} \frac{d a_{ij}}{dK}), \quad (5.45)$$

$$\frac{d a_{ij}}{dK} = \frac{\partial a_{ij}}{\partial T} \frac{dT}{dK} .$$
 (5.46)

When tracing critical lines in regions where no data are available to indicate whether or not critical points actually exist, it is useful to be able to compute the mathematical condition for stability, i.e., that the quartic form is positive. The quartic form for the TCC EOS was evaluated by taking the directional derivative of the cubic form along the critical displacement vector; that is, apply the operator

$$\frac{d}{dn} \equiv \sum_{i=1}^{C} Z_i \frac{\partial}{\partial n_i}$$
(5.47)

to eq (5.20). The result is

$$N^{3} \frac{dC}{dn} = RT \left[2 \sum_{i=1}^{c} \frac{N^{3} z_{i}^{4}}{n_{i}^{3}} + 8\overline{z}\overline{\beta}^{3} F_{1}^{3} + 6 \overline{\beta}^{4} F_{1}^{4} \right] + \frac{a}{b} \left[12 (\overline{a}\overline{\beta}^{2} - 2 \overline{a}\overline{\beta}^{3} + \overline{\beta}^{4})(\overline{F}_{3} + \overline{F}_{6}) - 8 (2 \overline{a}\overline{\beta}^{3} - \overline{\beta}^{4}) F_{4} + 6 \overline{\beta}^{4} F_{9} \right].$$
(5.48)

5.1 Functions of the Dimensionless Volume K and Their First Order Derivatives

Let $\Delta \equiv \delta_1 - \delta_2$, then

$$\begin{split} F_{1} &= 1/(K-1) \ , \\ F_{2} &= \frac{2}{\Delta} \left(\frac{\delta_{1}}{K+\delta_{1}} - \frac{\delta_{2}}{K+\delta_{2}} \right) \ , \\ F_{3} &= \frac{1}{\Delta} \left[\left(\frac{\delta_{1}}{K+\delta_{1}} \right)^{2} - \left(\frac{\delta_{2}}{K+\delta_{2}} \right)^{2} \right] \\ F_{4} &= \frac{1}{\Delta} \left[\left(\frac{\delta_{1}}{K+\delta_{1}} \right)^{3} - \left(\frac{\delta_{2}}{K+\delta_{2}} \right)^{3} \right] \\ F_{9} &= \frac{1}{\Delta} \left[\left(\frac{\delta_{1}}{K+\delta_{1}} \right)^{4} - \left(\frac{\delta_{2}}{K+\delta_{2}} \right)^{4} \right] \\ F_{5} &= \frac{2}{\Delta} \ln \left(\frac{K+\delta_{1}}{K+\delta_{2}} \right) \ , \\ F_{6} &= F_{2} - F_{5} \ , \end{split}$$

and their first order derivatives $\frac{dF_{i}}{dK}$ = F_{Ki} are

$$F_{K1} = -F_1^2,$$

$$F_{K2} = \frac{2}{\Delta} \left[-\frac{\delta_1}{(K+\delta_1)^2} + \frac{\delta_2}{(K+\delta_2)^2} \right]$$

$$F_{K3} = \frac{2}{\Delta} \left[-\frac{\delta_1^2}{(K+\delta_1)^3} + \frac{\delta_2^2}{(K+\delta_2)^3} \right]$$

$$F_{K4} = \frac{3}{\Delta} \left[-\frac{\delta_1^{-3}}{(K+\delta_1)^4} + \frac{\delta_2^{-3}}{(K+\delta_2)^4} \right] ,$$

$$F_{K5} = -\frac{2}{(K+\delta_1)(K+\delta_2)} ,$$

$$F_{K6} = F_{K2} - F_{K5} .$$

6. How to Use the Critical Point Software

Two subroutines have been written to compute critical points. CUBCR3 uses a quasi-Newton volume iteration and CUBCRPT uses a Newton-Raphson volume iteration in which the volume derivative of the cubic form is evaluated analytically (eq. 5.37). The calling arguments are the same for either of these subroutines, i.e.,

CALL CUBCRPT (NTYPE, NC, MXC, XN, T, P, V, IPR, CONV).

On entry,

	NTYPE	specifies type of TCC EOS. Current options are:
		1 for SRK EDS (Soave [13])
		2 for PR EOS (Peng and Robinson [10])
	NC	# of mixture components
	MXC(I)	identification number for each mixture component. The identification number
		corresponds the position of the component's data in the arrays in subroutine
		CUBDAT. Check a source listing to determine the pure components currently
		available.
	XU(I)	mole numbers (n, n ₂ ,, n _c).
	ī	initial guess of critical temperature (K). If set to 0.0 an initial guess is
		made internally.
	-7 a	initial guess of critical volume (cm ³). If set to 0.0 an initial guess is made
		internally.
	IPR	print flag for debugging. Set to 0 for no output. Set to 1 for summary of
		iterations written to unit 6.
Dn r	eturn,	
	Т	critical temperature (K)
	2	critical pressure (bar)
	7	critical volume (cm ³)
	CONV	convergence flag (logical).
		= .TRUE. if convergence achieved
		= .FALSE. if iteration fails
Exte	ernals,	
		CUBPROP: CUBDAT, FVOL, STABLIM, CUBMXT, CSUM, CFORM, SLDTK, DZK, ZKSUM, DCK,

CUBPROP: CUBDAT, FVOL, STABLIM, CUBMXT, CSUM, CFORM, SLDTK, DZK, ZKSUM, DCK, CUBMX, CUBP. LAS: SUMVC, DOT FORTRAN: DABS, DSIGN Usage: The variables XN, T, P, and V are double precision. The subroutines which must be linked to the driver are located in the following files: CUBCRIT, CUBPROP, BIP, DSPMAT, and LAS.

The software is structured so that all the pure component data that are required to compute a mixture critical point are contained in subroutine CUBDAT. This scheme allows the user to simply specify a set of identification numbers for the mixture components, and the number of moles, of each component in order to compute a critical point. However, to determine the critical point of a mixture containing a component (or components) for which the pure component data are not contained in CUBDAT, one must modify the software to include the required data. The pure component data which are required for each mixture component are: a critical temperature (K), critical pressure (bar), and the acentric factor. The arrays in CUBDAT should be dimensioned as follows:

PARAMETER (N=# of pure components whose data are stored in CUBDAT, NX=N*(N+1)/2) DOUBLE PRECISION PC(N), TTC(N), W(N), XI(NX)

In addition to the pure component data, any binary interaction coefficients (ξ_{ij}) which are not 1.0 are set in the subroutines SRKBIP (for the SRK EOS) or PRBIP (for the PR EOS). Just follow the example of the values already set there.

Storage for all arrays which may be variably dimensioned, depending on the number of mixture components, is set in subroutine CUBCRPT or CUBCR3. The proper dimensions are the following:

PARAMETER (N=# of mixture components, N1=N+1, NX=N* N1/2)
INTEGER KPVT(N)
DOUBLE PRECISION AIJ(NX), AIJT(NX), AIT(N), ALI(N), ATIJ(NX), AW(N), BI(N), BEI(N),
Q(NX), QA(N1,N), TCA(N), VCA(N), Z(N), ZK(N1), ZZ(N)

6.1 Verification of the Software

The accuracy of the software was verified by a twofold procedure:

- the results of a binary critical point calculation were compared to results obtained from an independent code which solved the traditional critical point equations of Gibbs;
- 2) the software was checked for internal consistency by comparing selected values of derivatives which are computed using the formulas given in this note, with the values obtained using different formulas.

Calculation of binary critical points was done for the $nC_{16}-CO_2$ mixture using the Peng and Robinson equation of state. A detailed consideration of the phase diagram for $nC_{16}-CO_2$ as predicted by the PR EOS, along with formulas for calculating critical points, can be found in Hong [16].

Figure 6.1 shows the result of a complete tracing of the critical line using a binary interaction coefficient $\zeta = 0.919$, and the following pure component data:

	nC ₁₆	C02
T _C (K)	717.0	304.21
P _C (MPa)	1.42	7.384
W	0.746	0.225



Figure 6.1 Calculated critical locus for the hexadecane + carbon dioxide system

The gas constant was set to 0.00831434 MPa·L/(mol·K). A benchmark result for $x(nC_{16}) = 0.99$ follows:

```
T<sub>c</sub> = 716.701292254 K
V<sub>c</sub> = 1.27759526809 L/mol
P<sub>c</sub> = 1.46980319713 MPa
```

The independent calculations both produced the above result to the accuracy presented.

The following consistency checks were performed on multi-component mixtures containing up to 12 components:

- Values of the cubic form computed using eq (4.10) were compared to values obtained from the "numerical" version, eq (4.11);
- Values of dT/dV computed using eq (4.18) were compared to values obtained from a difference formula;
- Values of dZ/dV obtained by solving the system of eq (4.24) were compared to values obtained from a difference formula;
- 4) Values of dC/dV computed using eq (4.20) were compared to values obtained from a difference formula.

Generally, 6 to 8 significant figures of agreement were obtained from these comparisons.

7. Summary of FORTRAN Subprograms

1) CUBDAT computes the temperature independent part of the pure component parameters and mixture cross terms. The calling sequence is CALL CUBDAT (NTYPE, NC, MXC, G, TCA, VCA, AIJ, AW, BI, R).

On entry,

NTYPE	specifies type of TCC EOS.	Current options are:	1	for	an	SRK EOS,	2	for	а	PR
	EOS.									
NC	# of mixture components.									
MXC(I)	identification # of each mi	xture component.								

On return,

G(I)	$G(1) = \delta_1, G(2) = \delta_2$
TCA(I)	critical temperatures (K) of pure mixture components
VCA(I)	critical molar volumes (cm ³ /mol) of pure mixture components
AIJ(IP)	upper triangular part of the symmetric matrix of ${\tt a_{ij}}$ packed by columns, i.e.,
	IP = i + j(j-1)/2. In unpacked notation,
	$AIJ(I,I) = \Omega_a R^2 T_{ci}^2 / P_{ci}$
	$AIJ(I,J) = \xi_{ij}[AIJ(I,I) * AIJ(J,J)]^{1/2}$
AW(I)	$= m(\omega_{1})$
BI(I)	= $\Omega_{\rm D}$ RT _{ci} /P _{ci}
R	gas constant = 0.00831434 MPa·L/(mol·K)

Externals,

BIP: SRKBIP, PRBIP FORTRAN: DSQRT Usage: CUBDAT is only called once for any set of critical point or stability limit calculations on a given mixture since it computes quantities which are independent of (T, V, n_i).

 CUBMX computes the temperature and composition dependent coefficients. The calling sequence is

CALL CUBMX (NC, T, XN, XNT, TCA, AIJ, AW, BI, ATIJ, ALI, BEI, A,B).

On entry,

NC	# of mixture components (c)
Т	temperature (T) in kelvins
XN(I)	mole numbers (n ₁ , n ₂ ,, n _c)
XNT	$N = \sum_{i=1}^{C} n_{i}$
TCA(I)	T _{ci}
AIJ(IP)	temperature independent part of a_{ij} ($\equiv a_{ij}^*$)
AW(I)	m (ω ₁)
BI	bi

On return,

ATIJ(IP) aij in packed storage of upper triangular part

ALI(I)	$\alpha_{i} = \frac{1}{Na} \sum_{j=1}^{C} n_{j} a_{ij}$
BEI(I)	$\beta_i = b_i / b$

A
$$a = \frac{1}{N^2} \sum_{i,j=1}^{c} n_i n_j a_i$$

 $B \qquad b = \frac{1}{N} \sum_{i=1}^{C} n_i b_i$

Externals,

FORTRAN: DSQRT Usage: CUBDAT must be called before CUBMX.

3) CUBMXT computes the temperature derivatives of the EOS coefficients. The calling sequence is

CALL CUBMXT (NC, T, XN, XNT, TCA, AIJ, AW, ATIJ, AT, AIT, AIJT).

On entry,

NC c T T

XN(I)	ni
XNT	N
TCA(I)	Tci
AIJ(IP)	a' _{ij}
AW(I)	m(ω _i)
ATIJ(IP)	a _{ij}

On return,

AT
$$\frac{dA}{dT} = \frac{1}{N^2} \sum_{i,j=1}^{C} n_i n_j \frac{da_{ij}}{dT}$$

AIT(I)
$$\frac{d (a\alpha_{i})}{dT} = \frac{1}{N} \sum_{j=1}^{C} n_{j} \frac{d a_{ij}}{dT}$$

AIJT(IP)
$$\frac{d a_{ij}}{dT} = \frac{a_{ij}}{2} \left[a_{ii}^{1} \frac{d a_{ii}}{dT} + a_{jj}^{1} \frac{d a_{jj}}{dT} \right]$$

where

$$\frac{d a_{ii}}{dT} = a_{ii}' \left\{ 1 + m_i \left[1 - \left(\frac{T}{T_{ci}}\right)^{1/2} \right] \right\} \left[\frac{-m_i}{(T T_{ci})^{1/2}} \right]$$

upper triangular part of symmetric matrix is stored in packed form.

Externals,

FORTRAN: DSQRT Usage: CUBDAT and CUBMX must be called before CUBMXT.

4) FVOL computes the functions of the dimensionless volume (V/Nb) and their 1st order derivatives. The calling sequence is

CALL FVOL (V, XNT, B, G, FV)

```
On entry,

V system volume (V) in cm<sup>3</sup>

XNT N

B b

G(I) G(1) = \delta_1, G(2) = \delta_2
```

On return,

FV(I)	$FV(1) = F_{1}$	$FV(2) = F_2$,	$FV(3) = F_3,$	$FV(4) = F_4$, F'	V(5)=F ₅ ,	$FV(6) = F_6$, $FV(7) = F_{k1}$,
	$FV(8) = F_{K2}$,	$FV(9) = F_{K3}$,	FV(10)=F _{K4}	, $FV(11) = F_{K}$	5, FV(12)	=F _{K6} , FV	(13)=Fg

Externals,

FORTRAN: DLOG

Usage: CUBDAT must be called before FVOL. The argument B may be supplied either by a call to CUBMX or simply by summing:

$$b = \frac{1}{N} \sum_{i=1}^{C} n_i b_i$$

5) CUBP is a double precision function which returns the pressure. The calling sequence is

```
P = CUBP (T, VM, G, A, B, R)
```

On entry,

Т	T (K	()
MV	V/N	(cm3/mol)
G(I)	δ1,	δ2
А	а	
В	b	
R	gas	constant

On return,

CUBP system pressure (P) in bar Usage: CUBDAT and CUBMX must be called before CUBP.

6) CUBDPV is a double precision function which returns $\frac{dP}{dV}$)_{T.N}.

DPV = CUBDPV (T, VM, G, A, B, R). The argument list is identical to that for CUBP.

7) CUBF computes fugacity. The calling sequence is CALL CUBF (I, T, V, XN, XNT, G, A, B, ALI, BEI, F, R)

On entry,

I	index for mixture component i
Т	Т
V	V
XN(I)	ni
XNT	N
G(I)	δ1, δ2
А	а
В	b
ALI(I)	αi
BEI(I)	βi
R	gas constant R

On return,

F RT ln f_i

Externals, FORTRAN: DLOG Usage: CUBDAT and CUBMX must be called before CUBF 8) QIJ computes matrix element q_{ij} . The calling sequence is CALL QIJ (I, J, T, FV, XN, XNT, ATIJ, A, B, ALI, BEI, Q, R) On entry, I index for mixture component i J index for mixture component j Т Т FV(I) F_i, F_{Ki} XN(I) ni XNT N ATIJ(IP) aij (packed storage) А а В b ALI(I) α_i BEI(I) β_i R gas constant

On return,

Q RT
$$\frac{\partial \ln f_i}{\partial n_i}$$

Usage: CUBDAT, CUBMX, and FVOL must be called before QIJ. This routine is called by PAKQ to assemble Q.

9) PAKQ assembles the upper triangular part of the symmetric Q matrix into packed form. the calling sequence is CALL PAKQ (NC, T, FV, XN, XNT, Q, ATIJ, A, B, ALI, BEI, R)

On entry,

NC	# of mixture components
Т	Т
FV(I)	F_{i} and F_{Ki}
X11(I)	n _i
XNT	Ν
ATIJ(IP)	a _{ij}
А	а
В	Ъ
ALI(I)	ai
BEI(I)	βi
R	gas constant

On return,

Q(IP) packed Q

Externals,

CUBPROP: QIJ

Usage: CUBDAT, CUBMX, and FVOL must be called before PAKQ. PAKQ is called by DETQ which computes Δ , and by DZK which computes Z_{K} .

10) DETQ assembles Q by calling PAKQ, then computes its determinant using the LINPACK routines DSPFA and DSPDI. A flag can be set to indicate that the null vector is to be computed, in which case DSPCO is called instead of DSPFA. The null vector is normalized to unit length. The calling sequence is CALL DETQ (NC, T, FV, XN, XNT, Q, KPVT, Z, INL, RCOND, DTQ, ATIJ, A, B, ALI, BEI, R)

On entry,

On

	NC	# of mixture components
	Т	T
	FV(I)	F_i and F_{Ki}
	XN(I)	ni
	XNT	N
	INL	null vector computation flag:
		INL = 0 for no null vector computation
		INL = 1 for null vector computation
		When INL is set to 1, it is assumed that the \underline{Q} matrix has already been
		determined to be singular.
	ATIJ(IP)	a _{ij}
	А	a
	В	b
	ALI(I)	α_1
	BEI(I)	β _i
	R	gas constant
On re	eturn,	
	Q(IP)	information from the factorization of \underline{Q} by DSPFA or DSPCO
	KPVT(I)	array used by LINPACK routines to store pivot information
	Z(I)	null vector components \textbf{Z}_{1} . Z(I) is computed by LINPACK routine DSPCO, and
		contains an approximate null vector when $\underline{\mathbb{Q}}$ is nearly singular, i.e., when the
		reciprocal condition number is on the order of machine roundoff.
	RCOND	reciprocal condition number computed by DSPCO
	DTQ	A≡det <u>Q</u> computed by DSPDI
Exter	nals,	

CUBPROP: PAKQ LINPACK: DSPCO, DSPFA, DSPDI

FORTRAN: IDINT, DSQRT Usage: CUBDAT, CUBMX, and FVOL must be called before DETQ. This routine is called by QNT to find T on the stability limit, then compute Z. 11) QNT performs the quasi-Newton iteration on temperature to solve $\Delta(T) \equiv \det |Q| = 0$ for a given volume. The calling sequence is CALL QNT (NC. T, FV, XN, XNT, RDT, TOLT, ITMX, IPR, IT, IFT, Q, KPVT, Z, TCA, AIJ, AW, ATIJ, BI, ALI, BEI, R) On entry, NC # of mixture components Т initial guess of $T(T_0)$ FV(I) F; and FK; XN(I) ni XNT Ν RDT $\delta T/T$ where δT is the increment used to compute the derivative $\partial \Delta (T_0)/\partial T$ TOLT iteration convergence tolerance $|T_{i+1} - T_i|/T_i < TOLT$ ITMX maximum number of iterations IPR print flag: 0 for no printing 1 for printing of iteration progress on unit 6 TCA(I) Tci AIJ(IP) a'ij $m(\omega_i)$ AW(I) BI(I) bi R gas constant On return, Т temperature on stability limit ($\Delta=0$) number of iterations to convergence IT iteration flag: IFT 0 successful iteration 1 iteration failed Q(IP) factored Q (from DSPFA) KPVT(I) pivots (LINPACK routines) Z(I)not used

ATIJ(IP) a_{ij} at T on stability limit

ALI(I) α_i at T on stability limit BEI(I) β_i

Externals,

CUBPROP: CUBMX, DETQ FORTRAN: DABS, DSIGN Usage: CUBDAT and FVOL must be called before QNT. CUBMX and DETQ are called from within the iteration loop on temperature in QNT. This routine is called by STABLIM.

12) STABLIM locates the temperature on the stability limit when the volume is fixed. Then the null vector is computed. On the 1st call to STABLIM the direction of \underline{Z}_1 is determined by requiring $Z_1 > 0$. On subsequent calls to STABLIM, for a given critical point or stability limit calculation, the direction of \underline{Z}_1 is determined by requiring $\underline{Z}_{i-1}^T \underline{Z}_i > 0$. The calling sequence is CALL STABLIM (NC, T, FV, XN, XNT, RDT, TOLT, ITMX, IPR, IT, IFT, IFC, Q, KPVT, Z, ZZ, TCA, AIJ, AW, ATIJ, BI, ALI, BEI, A, B, R)

On entry,

On r

NC	# of mixture components
Т	initial guess of T on stability limit
FV(I)	F_i and F_{Ki}
XN(I)	n _i
XNT	N
RDT	$\delta T/T,$ where δT is the increment used to compute the derivative $\partial \Delta(T_O)/\partial T$
TOLT	iteration convergence tolerance, i.e.,
	$ T_{i+1} - T_i / T_i < TOLT$
ITMX	maximum number of iterations
IPR	iteration print flag:
	0 for no printing
	1 for printing of iteration progress on unit 6
IFC	first call flag
	1 first call; set $Z_1 > 0$
	0 not first call; require $\underline{Z}_{i-1}^{T} \underline{Z}_{i} > 0$
TCA(I)	T _{ci}
AIJ(IP)	a'ij
AW(I)	$m(\omega_i)$
BI(I)	^b i
R	gas constant
return,	
i	temperature on stability limit
	# of iterations for convergence
TEL	Iteration convergence flagnot currently usedif iteration fails in QNT,
0(10)	execution is stopped in STABLIM.
Q(IP)	ractored Q (irom DSPCO)
RPVI(1)	pivol information (from DSPCO)
Z(1)	$\frac{2}{1}$
	$\underline{2}_{i-1}$ (from previous iteration on volume)
ALIJ(IP)	aj
ALI(I)	α _i

BEI(I) β_i A a B b

Externals,

```
CUBPROP: QNT, CUBMX, DETQ
FORTRAN: DABS
Usage: CUBDAT and FVOL must be called before STABLIM.
```

13) ZSUM computes the summations involving the null vector components which are used to compute the quadratic, cubic, and quartic forms. The calling sequence is CALL ZSUM (NC, XN, XNT, Z, ATIJ, ALI, BEI, A, AIT, AIJT, ZS)

On entry,

NC	# of mixture components (c)
XN(I)	n _i
XNT	Ν
Z(I)	null vector components (Z_1, Z_2, \ldots, Z_c)
ATIJ(IP)	a _{ij} (packed storage)
ALI(I)	α _i
BEI(I)	βi
А	a
AIT(I)	$d(a\alpha_i)/dT$
AIJT(IP)	d(a _{ij})/dT (packed storage)

On return,

$$ZS(I) \qquad ZS(1) = \sum_{i=1}^{c} \frac{Z_{i}^{2}}{y_{i}} \text{ where } y_{i} \equiv \frac{n_{i}}{N}$$

$$ZS(2) = \sum_{i=1}^{c} \frac{Z_{i}^{3}}{y_{i}^{2}}$$

$$ZS(2) = \sum_{i=1}^{c} \frac{Z_{i}^{4}}{y_{i}^{3}}$$

$$ZS(9) = \sum_{i=1}^{c} \frac{Z_{i}}{y_{i}^{3}}$$

$$ZS(3) = \overline{Z} = \sum_{i=1}^{c} Z_{i}$$

$$ZS(4) = \overline{\beta} = \sum_{i=1}^{c} \beta_{i}Z_{i}$$

$$ZS(5) = \overline{\alpha} = \sum_{i=1}^{C} \alpha_i Z_i$$
$$ZS(6) = \overline{a} = \frac{1}{a} \sum_{i,j=1}^{C} a_{ij} Z_i Z_j$$
$$ZS(7) = \overline{\alpha}_T = \sum_{i=1}^{C} \frac{d(a\alpha_i)}{dT} Z_i$$
$$ZS(8) = \overline{a}_T = \sum_{i,j=1}^{C} \frac{da_{ij}}{dT} Z_i Z_j$$

Usage: CUBDAT, FVOL, STABLIM, and CUBMXT must be called before ZSUM.

14) QFORM computes the quadratic form. The calling sequence is CALL QFORM (XNT, R, T, A, B, ZS, FV, QF)

On entry,

XNT	Ν
R	gas constant
Т	temperature on stability limit
А	a
В	b
ZS(I)	sums involving \underline{Z}
FV(I)	F_i and F_{Ki}

On return,

QF $\underline{Z}^{T} \underline{Q} \underline{Z}$

Usage: CUBDAT, FVOL, STABLIM, CUBMXT, and ZSUM must be called before QFORM.

15) CFORM computes the cubic form. The calling sequence is CALL CFORM (XNT, R, T, A, B, ZS, FV, CF)

On entry,

Same as QFORM

On return,

CF

$$\sum_{i,j,k=1}^{c} \frac{\partial^{3}A}{\partial n_{i} \partial n_{j} \partial n_{k}} Z_{i} Z_{j} Z_{k}$$

Usage: same as QFORM

16) DFORM computes the quartic form. The calling sequence is

CALL DFORM (XNT, R, T, A, B, ZS, FV, DF)

On entry, same as QFORM.

On return,

DF
$$\sum_{i,j,k,l=1}^{C} \frac{\partial^{4}A}{\partial n_{i} \partial n_{j} \partial n_{k} \partial n_{l}} Z_{i} Z_{j} Z_{k} Z_{l}$$

Usage: same as QFORM.

17) SLDTK computes dT/dK along the stability limit. The calling sequence is CALL SLDTK (R, T, A, B, AT, ZS, FV, DTK)

On entry,

R	gas constant
T	Т
А	a
В	b
AT	da∕dT
ZS(I)	sums involving \underline{Z}
FV(I)	F_{i} and F_{Ki}

On return,

DTK dT/dK

Usage: CUBDAT, FVOL, STABLIM, CUBMXT, and ZSUM are called before SLDTK.

18) QKMAT assembles the upper triangular part of the symmetric matrix $d\underline{Q}/dK$ in packed form. The calling sequence is CALL QKMAT (NC, T, FV, XN, XNT, QK, ATIJ, A, B, ALI, BEI, AT, AIT, AIJT, DTK, R)

On entry,

NC	# of mixture components
Т	temperature on stability limit
FV(I)	F_i and F_{Ki}
XN(I)	n _i
XNT	N
ATIJ(IP)	a _{ij}
A	а
В	b
ALI(I)	α _i
BEI(I)	ßi
AT	da/dT
AIT(I)	d(aa _i)/dT
AIJT(IP)	d a _{ij} /dT
DTK	dT/dK

gas constant R

On return,

```
QK(IP) d\underline{Q}/dK = \partial\underline{Q}/\partial K + (\partial\underline{Q}/\partial T)(dT/dK)
Usage: CUBDAT, FVOL, STABLIM, CUBMXT, ZSUM, and SLDTK must be called before QKMAT
```

19) DZK computes dZ/dK along the stability limit. In assembling the rectangular matrix, the bottom row (Z^{T}) is scaled so that the largest component of Z is the same magnitude as the largest component of Q. The rectangular system is solved using a simple Gaussian elimination algorithm with partial pivoting, i.e, row exchanges only. Thus, at some point in the elimination sequence, a zero pivot is encountered (because \underline{Q} is singular) and the bottom row will be exchanged with the row containing that pivot. The elimination sequence is completed, and the back substitution proceeds as if the system were square. The calling sequence is CALL DZK (NC, T, FV, XN, XNT, Q, ATIJ, A, B, ALI, BEI, AT, AIT, AIJT, DTK, NC1, MQA, QA, Z, ZK, R)

On entry,

	NC	<pre># of mixture components (c)</pre>
	Т	temperature on stability limit
	FV(I)	F_i and F_{Ki}
	XN(I)	n _i
	XNT	N
	ATIJ(IP)	a _{ij}
	A	a
	В	b
	ALI(I)	α _i
	BEI(I)	β _i
	AT	da/dT
	AIT(I)	$d(a\alpha_i)/dT$
	AIJT(IP)	d a _{ij} /dT
	DTK	dT/dK
	NC1	c+1
	MQA	1st dimension of QA array
	QA(I,J)	work space used for rectangular matrix. Must be dimensioned at least QA (NC1,
		NC)
	Z(I)	Zi
	R	gas constant
On r	eturn,	
	Q(IP)	2
	ZK(I)	dZ ₁ /dK
Exte	rnals,	

CUBPROP: PAKQ, QKMAT LAS: MSAX, RMSOL FORTRAN: DABS Usage: CUBDAT, FVOL, STABLIM, CUBMXT, ZSUM, and SLDTK must be called before DZK.

20) ZKSUM computes the sums involving $\rm Z_{Ki}$. The calling sequence is CALL ZKSUM (NC, XN, XNT, Z, ZK, ATIJ, A, ALI, BEI, ZS, DTK, ZKS)

On entry,

NC	# of mixture components
XN(I)	n _i
XNT	Ν
Z(I)	Zi
ZK(I)	Z _{Ki}
ATIJ(IP)	a _{ij}
А	a
ALI(I)	α _i
BEI(I)	β _i
ZS(I)	sums involving Z _i
DTK	dT/dK

On return,

$$ZKS(I) \qquad ZKS(1) = \sum_{i=1}^{c} \frac{Z_{i}^{2} Z_{Ki}}{y_{i}^{2}} \text{ where } y_{i} = \frac{n_{i}}{N}$$

$$ZKS(2) = \overline{Z}_{K} = \sum_{i=1}^{c} Z_{Ki}$$

$$ZKS(3) = \overline{\beta}_{K} = \sum_{i=1}^{c} \beta_{i} Z_{Ki}$$

$$ZKS(4) = (\overline{aa})_{K} = \sum_{i=1}^{c} [a\alpha_{i} Z_{Ki} + Z_{i} \frac{\partial(a\alpha_{i})}{\partial T} \frac{dT}{dK}]$$

$$ZKS(5) = (\overline{aa})_{K}$$

$$= \sum_{i,j=1}^{c} [(Z_{Ki}Z_{j} + Z_{i}Z_{Kj}) a_{ij} + Z_{i}Z_{j} \frac{\partial}{\partial T} \frac{dT}{dK}]$$

Usage: CUBDAT, FVOL, STABLIM, CUBMXT, ZSUM, SLDTK, and DZK must be called before ZKSUM.

21) DCK computes the derivative of the cubic form along the stability limit. The calling sequence is CALL DCK (XNT, R, T, DTK, A, B, AT, ZS, FV, ZKS, CK)

On entry,

XNT	N
R	gas constant
Т	temperature on stability limit
DTK	dT/dK
A	а
В	b
AT	da/dT
ZS(I)	sums involving Z
ZKS(I)	sums involving Zk

On return,

CK dC/dK

Usage: CUBDAT, FVOL, STABLIM, CUBMXT, ZSUM, SLDTK, DZK, and ZKSUM must be called before DCK.

22) MSAX computes the product of a symmetric matrix and a vector. The calling sequence is

CALL MSAX (N, A, X, B)

On entry,

N	order of the matrix
A(IP)	upper triangular part of A stored in packed form, i.e., $A(J^*(J-1)/2+I) = A(I,J)$
X(I)	vector to be multiplied by $\underline{\mathbb{A}}$

On return,

B(I) result A X = B

23) SUMVC sums the components of a vector. The calling sequence is CALL SUMVC (N,X,S)

On entry,

N	size of vector			
X(I)	vector	to be	summed,	x

On return,

S

∑ X_i i=1

24) DOT computes the dot product of two vectors. The calling sequence CALL DOT (N,X,Y,S)

On entry,

N size of vectors

X(I),Y(I) vectors to be dotted; X, Y

On return,

S

$$\sum_{i=1}^{N} X_{i}Y_{i}$$

25) RMSOL solves the rectangular system $\underline{A} \times \underline{X} = \underline{B}$, where A is an M × N matrix. It is assumed that M = N+1 and that a unique solution exists, i.e., the rank of A is N. The matrix is factored by Gaussian elimination with partial pivoting. The calling sequence is CALL RMSOL (NA, M, N, A, B)

On entry,

NA	1st dimension of the array A(I,J)
М	$\#$ of rows in $\underline{\mathbb{A}}$ (assumed to equal N+1)
Ν	# of columns in <u>A</u>
A(I,J)	matrix to be factored
B(I)	right hand side <u>B</u>

On return,

B(I) solution X

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ON THE CALCULATION OF CRITICAL POINTS BY THE METHOD OF HEIDEMANN AND KHALIL				
Brian E. Eaton				
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Document describes a	a computer program; SF-185, F1P	S Software Summary, is attached.		
11. ABSTRACT (A 200-word o	or less factual summary of most s	significant information. If docume	nt includes a significant	
The formulation of critical point criteria by Heidemann and Khalil is analyzed and contrasted with the original formulation of Gibbs. An extension to the solution technique originally used by Heidemann and Khalil, and later improved by Michelsen and Heidemann, is presented along with its detailed implementation for a general two-constant cubic equation of state. Finally, FORTRAN software developed for these computations is carefully documented.				
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