Critical Point Criteria in Legendre Transform Notation

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Legendre transform theory is used to develop two general critical point criteria for a classical thermodynamic system. The problem of indeterminancy is discussed, as is the option of employing mole fractions (rather than mole numbers).

SCOPE

"It has been ascertained by experiment that the variations of two coexisting states of the same substance are in some cases limited in one direction by a terminal state at which the distinction of the coexistent states vanishes. This state has been called the *critical state*." Gibbs presented this definition in his pioneering paper "On the Equilibrium of Heterogeneous Substances" in 1876. He then proceeded to show that this definition implies certain mathematical relationships between thermodynamic properties at the critical point. His results have been extensively quoted in the past century.

Gibbs stated the critical point criteria with only three sets of independent thermodynamic variables. Others have transformed his criteria to different variable sets when such a step expedited numerical computation, but, to our knowledge, no one has examined the general criteria.

Legendre transforms provide an opportunity to restate the Gibbs criteria in a more coherent and more flexible form. The development of critical point criteria in Legendre transform notation is, therefore, the subject of this paper.

CONCLUSIONS AND SIGNIFICANCE

Extending the stability analysis of Beegle et al. (1974*a*, *b*), we derive the two necessary and sufficient critical point criteria in terms of two partial derivatives of the n^{th} Legendre transform, where n is the number of components present in the system [Equations (2) and (7)]. These two single derivatives are then shown to be equivalent to null determinants [Equations (13) through (16)] when lower-order Legendre transforms are employed. With these results, it is now possible to select any combination of independent variables from the fundamental equation and immediately write the necessary and sufficient critical point relations. Several examples are shown.

The derivation was carried out by employing mole numbers as variables, as did Gibbs in his work. Nevertheless, most recent authors have used mole fractions instead. There is, however, no general one-to-one correspondence between extensive thermodynamic derivatives with respect to mole numbers and intensive derivatives with respect to mole fractions. The general problem of employing intensive critical point criteria is examined, and it is shown that a direct substitution is only valid for particular Legendre transforms. The proof involves the expansion of the total internal energy of a system in terms of total entropy, total volume, total moles, and mole numbers of all components but one.

When applying critical point criteria to real systems, Gibbs anticipated, and others have demonstrated, that the formulation could involve an indeterminate form where the numerator and denominator both approach zero simultaneously. A physical picture is given to describe this problem, and a simple modification of the criteria is suggested to overcome the indeterminancy.

All derivations are made assuming a classical fluid, the properties of which may be expanded in a Taylor series around the critical point. While recent data indicate that there are anomalies in many thermodynamic derivatives close to the critical point (Levelt Sengers, 1970; Levelt Sengers et al., 1976; Griffiths and Wheeler, 1970; Chapela and Rowlinson, 1974; Hicks and Young, 1975; Hall and Eubank, 1976; Scott, 1972), the results obtained by the classical approach are valid when gas-liquid or liquid-liquid critical points are to be estimated or correlated with data using analytical expressions for the thermodynamic functions.

THEORY

Beegle et al. (1974*a*, *b*) presented a criterion to define the limit for the stability for thermodynamic systems and employed Legendre transforms in the development. Heidemann (1975) illustrated the fact that such a criterion was limited to testing stable systems as they approached the limit of stability.

The principal result of Beegle et al. was to show that for a stable n-component system

$$y^{(n)}_{(n+1)(n+1)} > 0 \tag{1}$$

and a system reaches the limit of stability, that is, lies on

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the spinodal curve, when

$$\overset{(n)}{y}_{(n+1)(n+1)} = 0 \tag{2}$$

$y^{(n)}$ is the n^{th} order Legendre transform, and $\overset{(n)}{y}_{(n+1)(n+1)}$ is the second-order partial derivative with respect to the extensive variable x_{n+1}; the derivative is obtained at constant values of $\xi_1, \xi_2, \ldots, \xi_n, x_{n+2}$. ξ_i is an intensive variable and is the partial derivative of the zero$^{\text{th}}$ order Legendre transform, that is, the base function $y^{(0)} = f(x_1, x_2, \ldots, x_{n+2})$, with respect to x_i. For additional detail, refer to Beegle et al. (1974*a*, *b*).

Equations (1) and (2) are of value in specifying the conditions when a single-phase system, initially stable, becomes unstable with the concomitant formation of a new phase. A convenient physical picture related to this problem is give by Modell and Reid (1974) and is briefly described so as to provide a base to define a critical state.

As noted following Equation (2), the condition for a thermodynamic state to exist on the spinodal curve is that $\overset{(n)}{y}_{(n+1)(n+1)} = 0$. We then have a single-phase system which is maintained at constant intensive properties $\xi_1, \xi_2, \ldots, \xi_n$ by some external means, and, also, the total value of the extensive parameter x_{n+2} is constant.

We illustrate these concepts with a ternary system and order the independent variables such that

$$\begin{gathered} y^{(0)} = \underline{U} = f(x_1, x_2, \ldots, x_5) = f(\underline{S}, \underline{V}, N_1, N_2, N_3) \\ x_1 = \underline{S}, \quad x_2 = \underline{V}, \quad x_3 = N_1, \quad x_4 = N_2, \quad x_5 = N_3 \end{gathered} \tag{3}$$

$$\begin{aligned} y^{(n)} = y^{(3)} &= y^{(0)} - \xi_1 x_1 - \xi_2 x_2 - \xi_3 x_3 \\ &= \underline{G}' = \underline{U} - T\underline{S} + P\underline{V} - \mu_1 N_1 \end{aligned} \tag{4}$$

that is, $\xi_1 = T$, $\xi_2 = -P$, $\xi_3 = \mu_1$, etc., and

$$\overset{(n)}{y}_{(n+1)(n+1)} = \overset{(3)}{y}_{44} = (\partial^2 \underline{G}'/\partial N_2{}^2)_{T,P,\mu_1,N_3} \tag{5}$$

With the ordering of variables as noted above, to test the stability of this system we must vary N_2 yet maintain T, P, μ_1, and N_3 constant. To carry out such a test, we suggest a simple thought experiment wherein we divide our system into two hypothetical regions which we call α and β. Initially, all intensive properties are identical in both α and β. Now we separate α from β by a membrane this is diathermal, movable, and permeable to components 1 and 2. The membrane does not allow passage of component 3. Focus on subsystem α. We wish to test for the positive character of $\overset{(n)}{y}_{(n+1)(n+1)}$ [or $\overset{(3)}{y}_{44}$ in our example] by varying the quantity of x_{n+1} subject to the constraint that

$$dx_{n+1}(\alpha) + dx_{n+1}(\beta) = 0 \tag{6}$$

or, for the example

$$dN_2(\alpha) + dN_2(\beta) = 0$$

On the spinodal curve (approached from a stable phase), $\overset{(n)}{y}_{(n+1)(n+1)} = 0$ in both α and β. This must be true, since α and β are identical in the original formulation. To determine the effect of interchanging additional $x_{n+1}(N_2)$ for a system on the spinodal curve, we must consider the derivative $\overset{(n)}{y}_{(n+1)(n+1)(n+1)}$. If this derivative were positive, and if $dx_{n+1}(\alpha) > 0$, then $\overset{(n)}{y}_{(n+1)(n+1)} > 0$ in subsystem α. That is, α is stable with respect to the transfer. However, with Equation (6), $\overset{(n)}{y}_{(n+1)(n+1)}(\beta) < 0$, and subsystem β has become unstable and must form a new phase. Similar, but opposite, conclusions are reached if $dx_{n+1}(\alpha) < 0$.

Should there be a state on the spinodal that satisfies Equation (2) and, in addition, is a stable state, then, clearly

$$\overset{(n)}{y}_{(n+1)(n+1)(n+1)} = 0 \tag{7}$$

Stable states on the spinodal curve, that is, those which satisfy Equations (2) and (7), are termed critical states. If the critical state is to be a stable state, then

$$\overset{(n)}{y}_{(n+1)(n+1)(n+1)(n+1)} \geqq 0 \tag{8}$$

and if $\overset{(n)}{y}_{(n+1)(n+1)(n+1)(n+1)}$ is zero, then the lowest even-order, nonvanishing derivative of $y^{(n)}$ must be positive, and all lower-order derivatives must be zero.

The second critical criterion, Equation (7), also may be written

$$\left(\frac{\partial^2 \xi_{n+1}}{\partial x^2_{n+1}}\right)_{\xi_1,\xi_2,\ldots\xi_n,x_{n+2}} = 0 \tag{9}$$

For the ternary system used as an example earlier, Equation (2) has been given in Equation (5), and Equation (7) would be

$$\left(\frac{\partial^3 \underline{G}'}{\partial N_2{}^3}\right)_{T,P,\mu_1,N_3} = 0 \tag{10}$$

or

$$\left(\frac{\partial^2 \mu_2}{\partial N_2{}^2}\right)_{T,P,\mu_1,N_3} = 0 \tag{11}$$

Heidemann (1975) has employed Equation (11) to estimate critical points in ternary liquid-liquid systems.

An additional simple example would be a pure-component system. If we order variables as in Equation (3), with $n = 1$, $y^{(1)} = \underline{A}$, and $x_1 = S$, $x_2 = \underline{V}$, and $x_3 = N$. Equations (2), (7), and (8) would then be

$$\left.\begin{aligned} A_{VV} &= -(\partial P/\partial \underline{V})_{T,N} = 0 \\ A_{VVV} &= -(\partial^2 P/\partial \underline{V}^2)_{T,N} = 0 \\ A_{VVVV} &= -(\partial^3 P/\partial \underline{V}^3)_{T,N} \geqq 0 \end{aligned}\right\} \tag{12}$$

THE CRITICAL POINT IN TERMS OF $\mathcal{L}_i$ AND $\mathcal{M}_i$ DETERMINANTS

The critical point criteria [Equations (2) and (7)] have been expressed in terms of the n^{th} order Legendre transform as this provides the simplest form, that is, a single partial derivative. For computational purposes, it is often more convenient to employ lower-order transforms. In Beegle et al. (1974*b*), it was shown that an equivalent form to Equation (2) was that

$$\mathcal{L}_i = 0 \tag{13}$$

where

$$\mathcal{L}_i = \begin{vmatrix} \overset{(i)}{y}_{(i+1)(i+1)} \overset{(i)}{y}_{(i+1)(i+2)} & \cdots\cdots & \overset{(i)}{y}_{(i+1)(n+1)} \\ \overset{(i)}{y}_{(i+2)(i+1)} & \cdots\cdots & \overset{(i)}{y}_{(i+2)(n+1)} \\ \vdots & & \vdots \\ \overset{(i)}{y}_{(n+1)(i+1)} & \cdots\cdots & \overset{(i)}{y}_{(n+1)(n+1)} \end{vmatrix} \tag{14}$$

where $0 \leqq i \leqq n$.

The comparable expression for Equation (7) is*

$$\mathcal{M}_i = 0 \tag{15}$$

where

$$\mathcal{M}_i = \begin{vmatrix} \overset{(i)}{y}_{(i+1)(i+1)} \overset{(i)}{y}_{(i+1)(i+2)} & \cdots\cdots & \overset{(i)}{y}_{(i+1)(n+1)} \\ \overset{(i)}{y}_{(i+2)(i+1)} & \cdots\cdots & \overset{(i)}{y}_{(i+2)(n+1)} \\ \overset{(i)}{y}_{(n)(i+1)} & \cdots\cdots & \overset{(i)}{y}_{(n)(n+1)} \\ \partial\mathcal{L}_i/\partial x_{i+1} & \cdots\cdots & \partial\mathcal{L}_i/\partial x_{n+1} \end{vmatrix} \tag{16}$$

As an example, consider an n-component system and order the variables as $\underline{U} = f(\underline{S}, \underline{V}, N_1, N_2, \ldots N_n)$. Choose $i = 2$. Then $y^{(2)} = \underline{G}$, the Gibbs energy. With Equations (13) through (16), the critical point criteria are

$$\mathcal{L}_2 = \begin{vmatrix} G_{11} & G_{12} & \cdots\cdots & G_{1,n-1} \\ G_{21} & G_{22} & \cdots\cdots & G_{2,n-1} \\ \vdots & \vdots & & \\ G_{n-1,1} & & \cdots\cdots & G_{n-1,n-1} \end{vmatrix} = 0 \tag{17}$$

$$\mathcal{M}_2 = \begin{vmatrix} G_{11} & G_{12} & \cdots\cdots & G_{1,n-1} \\ G_{21} & G_{22} & \cdots\cdots & G_{2,n-1} \\ \vdots & \vdots & & \vdots \\ G_{n-2,1} & & \cdots\cdots & G_{n-2,n-1} \\ \partial\mathcal{L}_2/\partial N_1 & & \cdots\cdots & \partial\mathcal{L}_2/\partial N_{n-1} \end{vmatrix} = 0 \tag{18}$$

where $G_{11} = \partial^2\underline{G}/\partial N_1^2$, etc.

Equations (17) and (18) are identical to the criteria given by Gibbs (1878). There are, however, many alternate but equivalent criteria, depending upon the ordering of the independent variables and upon the value of i. As a final example, consider a binary of 1 and 2, that is, $n = 2$. If $i = 2$, Equations (13) to (16) reduce to

$$G_{11} = G_{111} = 0 \tag{19}$$

where $G_{11} = (\partial^2\underline{G}/\partial N_1^2)_{T,P,N_2} = (\partial\mu_1/\partial N_1)_{T,P,N_2}$

$$G_{111} = (\partial^3\underline{G}/\partial N_1^3)_{T,P,N_2} = (\partial^2\mu_1/\partial N_1^2)_{T,P,N_2}$$

An equivalent set other than (19) would result if $\underline{i} = 1$. Here $y^{(1)} = \underline{A}$, the Helmholtz energy [when the ordering is as in Equation (3)]:

$$\mathcal{L}_1 = \begin{vmatrix} A_{VV}A_{V1} \\ A_{1V}A_{11} \end{vmatrix} = 0 \tag{20}$$

$$\mathcal{M}_1 = \begin{vmatrix} A_{VV} & A_{V1} \\ \partial\mathcal{L}_1/\partial\underline{V} & \partial\mathcal{L}_1/\partial N_1 \end{vmatrix} = 0 \tag{21}$$

or

$$\mathcal{L}_1 = A_{VV}A_{11} - A_{V1}^2 = 0 \tag{22}$$

$$\mathcal{M}_1 = A_{111}A_{VV}^2 - A_{VVV}A_{11}A_{V1} - 3A_{V11}A_{VV}A_{V1} + 3A_{VV1}A_{V1}^2 = 0 \tag{23}$$

With Equations (13) through (16) it is a simple matter to obtain the thermodynamic criteria at the critical point. They may be expressed in many equivalent forms, depending upon the choice of i and the ordering of variables in the fundamental equation $\underline{U} = f(\underline{S}, \underline{V}, N_1, \ldots N_n)$.

PREVIOUS INVESTIGATIONS

The basis for all critical point studies was laid by Gibbs (1878). By a logical argument similar to the one presented here, he derived Equations (17) and (18) and also showed, separately, the validity of Equations (13) and (15) for the case where $i = 0$. In the last 20 yr, several excellent books (Callen, 1960; Tisza, 1966) and many papers have been published which developed further these equations proposed by Gibbs.

Two fundamental papers appeared in 1962. Boberg and White derived Equations (17) and (18) in intensive form, that is, with specific Gibbs energy and mole fractions, employing an argument that at constant temperature and pressure, G must be a minimum function with variations in composition. These authors applied their determinants to binary and ternary systems to estimate critical and plait points for liquid systems. The Redlich and Kister (1948) correlation was used to relate the excess Gibbs energy of mixing to composition. These same authors suggest, but do not develop, the idea that critical point criteria may be obtained using coordinate systems other than T, P, and composition.

Redlich and Kister (1962) discussed the prediction of a gas-liquid critical locus for binary systems. They chose to begin with the two relations

$$(\partial \ln \phi_1/\partial z_1)_{T,P} + 1/z_1 = 0 \tag{24}$$

$$(\partial^2 \ln \phi_1/\partial z_1^2)_{T,P} - 1/z_1^2 = 0 \tag{25}$$

where ϕ_1 is the fugacity coefficient of component 1 and z_1 represents mole fraction. These equations result from Equation (19) when μ_1 is related to ϕ_1. To obtain relations more convenient to use with equations of state explicit in pressure, they convert Equations (24) and (25) to derivatives of the Helmholtz energy. Although they employ intensive properties and mole fractions, their results are equivalent to the $\mathcal{L}$ and $\mathcal{M}$ determinants given in Equations (20) and (21). In using their equations to predict the effect of composition on critical temperatures and pressures, they first obtain the limits $(\partial T/\partial z_1)$ and $(\partial P/\partial z_1)$ at the end points where $z_1 = 0, 1$. Then, by an interpolation method, they estimated the mixture T_c and P_c as a function of composition. The Redlich-Kwong (1949) equation of state was selected to illustrate the method and obtain numerical values. In a subsequent paper, Ackerman and Redlich (1963) used a very similar technique with the Benedict-Webb-Ruben equation of state. Arai and Saito (1970) modified slightly the interpolative scheme of Redlich and Kister to estimate critical temperatures and pressures of binary mixtures. In the three papers using the Redlich-Kister method, reasonably good predictions were achieved for the mixture critical temperature, but often poor results were obtained for critical pressures.

As computers became more efficient and more available, others have employed the same equations [(22) and (23), but in the intensive form] to estimate gas-liquid critical points for binary systems (Joffe and Zudkevitch, 1967; Hissong and Kay, 1970; Sarashina et al., 1974; Huron, 1976; Pak and Kay, 1972). In these studies, the B-W-R or some variation of the Redlich-Kwong equation of state was employed to relate pressure to the volume, temperature, and composition at the critical point. The Gibbs criteria [Equation (19)] or the Helmholtz criteria [Equa-

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* Supplementary material has been deposited as Document No. 03102 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 440 Park Ave. South, New York, N.Y. 10016 and may be obtained for $3.00 for microfiche or $5.00 for photocopies.

tions (22) and (23)] were introduced without proof and in the intensive form. Results varied; for hydrocarbon binaries, the mixture critical temperature was usually estimated to ±2°C and the mixture critical pressure to within 1 bar. These results, however, were obtained only by meploying interaction parameters which were optimized from experimental data (Pak and Kay, 1972). Also, computation techniques varied among investigators.

Spear et al. (1969, 1971) investigated the gas-liquid critical locus for both binary and ternary systems using the Helmholtz determinants in intensive form. The Redlich-Kwong equation of state was assumed. Peng and Robinson (1977) used their equation of state (Peng and Robinson, 1976) to calculate critical properties of multicomponent hydrocarbon (and related) mixtures. Interaction parameters were required only for hydrocarbon-nonhydrocarbon binaries. Their results appear to be more accurate than shown in any previous study.

In all the papers published to date that deal with gas-liquid critical loci, all but one [Boberg and White (1962)] assume the criteria as stated by Gibbs (1878), but with intensive Gibbs energies and mole fractions rather than extensive Gibbs energies and moles. As noted later, this interchange is correct. Each study has noted the advantages in converting the Gibbs determinants to equivalent expressions in the Helmholtz energy. This transformation is not readily accomplished by normal thermodynamic means, although the Legendre transform theory introduced earlier in this paper and in Beegle et al. (1974*a*, *b*) provides a convenient and rigorous way to move from one coordinate system to another. The different papers discussed above assume various equations of state explicit for pressure, and each suggests efficient computational algorithms. The results vary. Since binary mixture critical temperatures are, normally, almost linear in composition, invariably good results are reported between calculated and experimental values. For mixture critical pressures, which are often quite nonlinear in composition, no one equation of state was uniformly successful unless mixture interactions were obtained by regression of experimental critical data. Clearly, the choice of an appropriate equation of state that well fits both P-V-T-y data (and derivatives) near the critical point is most difficult.

The use of stability and critical point criteria to estimate liquid-liquid critical and plait points has received far less study. Boberg and White (1962) discuss the problems briefly. Scott (1949) examined the thermodynamics of high polymer solutions, and Scott and Von Konynenburg 1970) use the van der Waals equation to study the properties of solutions. Heidemann (1975) introduces Legendre transforms to investigate the plait point for ternary systems, that is, with $y_{44}^{(3)}$ and $y_{444}^{(3)} = 0$ [see Equations (2) and (7)]. A simple Gibbs excess energy function was assumed to develop the concepts. Problems in actually converging on the true plait point are discussed in Heidemann's paper and in articles by Heidemann and Mandhane (1973, 1975). In the latter, the NRTL and van Laar equations were employed to estimate Gibbs excess energies of mixing.

Teja and Rowlinson (1973) and Teja and Kropholler (1975) have predicted gas-liquid binary and ternary critical loci in a slightly different manner. Starting with Equations (22) and (23) in intensive form, they use an extended form of the corresponding states principle with a reference substance whose P-V-T properties are well known. One interaction parameter per binary is required. For simple systems, their approach does not differ greatly from those described above. However, they have also used this scheme for systems where the $T_c - P_c$ locus is interrupted by two liquid phases or where azeotropes persist into the critical region (in particular, carbon dioxide-alkane systems). Hicks and Young (1976) have extended this approach.

COMMENTS ON THE USE OF MOLE FRACTIONS IN THE $\mathcal{L}_i$ AND $\mathcal{M}_i$ DETERMINANTS

Throughout the paper and in the previous work by Beegle et al. (1974*a*, *b*), the independent set of variables for the internal energy U was total entropy $\underline{S}$, total volume $\underline{V}$, and all mole numbers $N_1, \ldots N_n$. This set of independent variables delineated the appropriate variables which had to be maintained constant in any derivative of $\underline{U}$ $[y^{(0)}]$ or other Legendre transform $y^{(i)}$. For example, in a ternary, with the variables ordered as in Equation (3), the Legendre transform $\underline{G}'$ was defined in Equation (4), and

$$\mathcal{L}_3 = y_{44}^{(3)} = (\partial^2\underline{G}'/\partial N_2{}^2)_{T,P,\mu_1,N_3} \tag{26}$$

$$\mathcal{L}_2 = \begin{vmatrix} y_{33}^{(2)} & y_{34}^{(2)} \\ y_{43}^{(2)} & y_{44}^{(2)} \end{vmatrix} = \begin{vmatrix} \left(\dfrac{\partial^2\underline{G}}{\partial N_1{}^2}\right)_{T,P,N_2,N_3} & \left(\dfrac{\partial^2\underline{G}}{\partial N_1 \partial N_2}\right) \\ \left(\dfrac{\partial^2\underline{G}}{\partial N_1 \partial N_2}\right) & \left(\dfrac{\partial^2\underline{G}}{\partial N_2{}^2}\right)_{T,P,N_1,N_3} \end{vmatrix} \tag{27}$$

etc.

Suppose, however, that Equation (26) had been written* as

$$\underline{U} = f(\underline{S}, \underline{V}, N_1, N_2, N) \tag{28}$$

where $N = \sum_j N_j$. With the same approach as used earlier, we would have reached the conclusion that $\mathcal{L}_i = \mathcal{M}_i = 0$ at the critical point. But, the definitions of $\mathcal{L}_i$ and $\mathcal{M}_i$ are slightly modified. For example, Equation (26) now becomes

$$\mathcal{L}_3 = y_{44}^{(3)} = (\partial^2\underline{G}^+/\partial N_2{}^2)_{T,P,\eta_1,N} \tag{29}$$

where

$$\underline{G}^+ = \underline{U} - T\underline{S} + P\underline{V} - \eta_1 N_1 \tag{30}$$

$$\eta_1 = (\partial\underline{U}/\partial N_1)_{\underline{S},\underline{V},N_2,N} = (\partial\underline{G}/\partial N_1)_{T,P,N_2,N} \tag{31}$$

Note the difference between η_1 and the chemical potential μ_1:**

$$\mu_1 = (\partial\underline{U}/\partial N_1)_{\underline{S},\underline{V},N_2,N_3} = (\partial\underline{G}/\partial N_1)_{T,P,N_2,N_3} \tag{32}$$

Equation (29) could also be written as

$$\mathcal{L}_3 = (1/N)(\partial^2 G^+/\partial z_2{}^2)_{T,P,\eta_1,N} \tag{33}$$

with

$$G^+ = \underline{G}^+/N$$

Thus, with N held constant, it is a simple matter to convert this derivative to one employing mole fractions.

A more useful example of this method results when $\mathcal{L}_2$ is determined using the ordering in Equation (28):

$$\mathcal{L}_2 = \begin{vmatrix} y_{33}^{(2)} & y_{34}^{(2)} \\ y_{43}^{(2)} & y_{44}^{(2)} \end{vmatrix} = \begin{vmatrix} \left(\dfrac{\partial^2\underline{G}}{\partial N_1{}^2}\right)_{T,P,N_2,N} & \left(\dfrac{\partial^2\underline{G}}{\partial N_1 \partial N_2}\right) \\ \left(\dfrac{\partial^2\underline{G}}{\partial N_1 \partial N_2}\right) & \left(\dfrac{\partial^2\underline{G}}{\partial N_2{}^2}\right)_{T,P,N_1,N} \end{vmatrix} \tag{34}$$

where the Legendre transform $\underline{G}$ (Gibbs energy) is the same in Equations (27) and (34). It is obvious that Equation (34) can be written as

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* Munster (1970) also suggests this type of ordering.

** It may be shown that for $\underline{i} \neq \underline{n}$, $\eta_i = \mu_i - \mu_n$.

$$\mathcal{L}_2 = \frac{1}{N}\begin{vmatrix} \left(\dfrac{\partial^2 G}{\partial z_1^2}\right)_{T,P,z_2} & \left(\dfrac{\partial^2 G}{\partial z_1 \partial z_2}\right) \\ \left(\dfrac{\partial^2 G}{\partial z_1 \partial z_2}\right) & \left(\dfrac{\partial^2 G}{\partial z_2^2}\right)_{T,P,z_1} \end{vmatrix} \tag{35}$$

where, in each derivative, z_3 varies to maintain the requirement that $\sum_j dz_j = 0$.

The $\mathcal{L}_i$ and $\mathcal{M}_i$ determinants may always be converted to a mole fraction form [for example, Equation (33) or Equation (35)], but only if the Legendre transform is $\underline{A}$, $\underline{H}$, or $\underline{G}$ does one avoid introducing modified chemical potentials η_1. If $\underline{A}$, $\underline{H}$, or $\underline{G}$ are used, the expansion shown in Equation (28) may be employed. As shown in Beegle et al. (1974*a*, *b*), the last variable in the ordering (N in this case) is always a constraint in every derivative used in stability theory. With such a constraint, for any extensive variable, it is easy to convert to an intensive form; that is, if $\underline{B}$ were an extensive variable, then, *with N constant*, $d\underline{B} = NdB$, $d^2\underline{B} = Nd^2B$, etc.

Finally, it is obvious that if one should wish to employ mole fractions as working variables to specify stability and critical point criteria, one should order variables as in Equation (28), although $\underline{S}$ and $\underline{V}$ may be interchanged and the particular mole number eliminated is not important.

To conclude, we summarize the convenient stability and critical point criteria for an n-component system when mole fractions are used. In all derivatives involving mole fractions, z_n is not constant:

$$\underline{U} = f(\underline{S}, \underline{V}, N_1, \ldots N_{n-1}, N)$$

(ordering of N_i is arbitrary)

$$\mathcal{L}_2 = 0 = \frac{1}{N}\begin{vmatrix} \left(\dfrac{\partial^2 G}{\partial z_1^2}\right)_{z_2,\ldots z_{n-1}} & \left(\dfrac{\partial^2 G}{\partial z_1 \partial z_2}\right) & \left(\dfrac{\partial^2 G}{\partial z_1 \partial z_{n-1}}\right) \\ \left(\dfrac{\partial^2 G}{\partial z_2 \partial z_1}\right) & \left(\dfrac{\partial^2 G}{\partial z_2^2}\right)_{z_1, z_3, \ldots z_{n-1}} & \left(\dfrac{\partial^2 G}{\partial z_2 \partial z_{n-1}}\right) \\ \vdots & \vdots & \vdots \\ \left(\dfrac{\partial^2 G}{\partial z_{n-1} \partial z_1}\right) & \cdot & \left(\dfrac{\partial^2 G}{\partial z_{n-1}^2}\right)_{z_1,\ldots z_{n-2}} \end{vmatrix} \tag{36}$$

(T, P, N are constant in each derivative)

$\mathcal{M}_2$ is the determinant constructed from $\mathcal{L}_2$ by replacing the bottom row by $(\partial\mathcal{L}_2/\partial z_j)_{z_1,\ldots z_{j-1}, z_{j+1},\ldots z_{n-1}}$, where j is the j^{th} column, and $\mathcal{L}_2$ and $\mathcal{M}_2$ are $(n-1)$ by $(n-1)$ determinants. If $\mathcal{L}_1$ were desired, with the ordering as shown, then

$$\mathcal{L}_1 = 0 = \frac{1}{N}\begin{vmatrix} \left(\dfrac{\partial^2 A}{\partial V^2}\right)_z & \left(\dfrac{\partial^2 A}{\partial V \partial z_1}\right) \cdots\cdots & \left(\dfrac{\partial^2 A}{\partial V \partial z_{n-1}}\right) \\ \left(\dfrac{\partial^2 A}{\partial z_1 \partial V}\right) & \left(\dfrac{\partial^2 A}{\partial z_1^2}\right)_{V, z_2,\ldots z_{n-1}} \cdot\cdot & \left(\dfrac{\partial^2 A}{\partial z_1 \partial z_{n-1}}\right) \\ \vdots & \vdots & \vdots \\ \left(\dfrac{\partial^2 A}{\partial z_{n-1} \partial V}\right) & \left(\dfrac{\partial^2 A}{\partial z_{n-1} \partial z_1}\right) \cdots\cdots & \left(\dfrac{\partial^2 A}{\partial z_{n-1}^2}\right)_{V, z_1,\ldots z_{n-2}} \end{vmatrix} \tag{37}$$

with T also constant.

$\mathcal{M}_1 = \mathcal{L}_1$ with the entry in the bottom of the first column replaced by $(\partial\mathcal{L}_1/\partial V)_{z_1,\ldots z_{n-1}}$ and each entry in the other $n-1$ columns replaced by $(\partial\mathcal{L}_1/\partial z_j)_{V, z_1,\ldots z_{j-1}, z_{j+1},\ldots z_{n-1}}$, where $1 \leqq j \leqq n-1$. In a similar manner, $\mathcal{L}_0$ and $\mathcal{M}_0$ may be written.

INDETERMINANCY

A stable thermodynamic system containing n components is defined as one where

$$y_{kk}^{(k-1)} > 0 \quad 1 \leqq k \leqq n+1 \tag{38}$$

but, as shown in Beegle et al. (1974*b*) and in the discussion following Heidemann (1975), when the unstable region is approached, the first of these derivatives to become zero occurs $k = n + 1$. This leads to the stability criterion given by Equation (2). In a graph of ξ_{n+1} vs. x_{n+1} at constant $\xi_1 \ldots \xi_n$, x_{n+2}, such a criterion allows one to construct the spinodal curve to separate stable from unstable conditions. Within the spinodal curve, on the unstable side, lie other envelopes which satisfy the criteria

$$y_{kk}^{(k-1)} = 0 \quad 1 \leqq k \leqq n \tag{39}$$

Heidemann (1975) shows the $y_{33}^{(2)}$ curves within the $y_{44}^{(3)}$ spinodal curve for a ternary system at constant T and P. Teja and Kropholler (1975) show the $y_{22}^{(1)}$ curve within the $y_{33}^{(2)}$ curve for a binary system.

As long as all $y_{kk}^{(k-1)}$ curves ($k \leqq n$) fall within the $y_{(n+1)(n+1)}^{(n)}$ curve, numerical computations are straightforward. Should, however, $y_{nn}^{(n-1)}$ become tangent to the spinodal curve at the critical (or any other point), then an indeterminancy results where $y_{(n+1)(n+1)}^{(n)}$ and $y_{nn}^{(n-1)}$ both become zero. This can most readily be seen from the relation between $y_{nn}^{(n-1)}$ and $y_{(n+1)(n+1)}^{(n)}$ as given by the step-down operation of Beegle et al. (1974*a*):

$$y^{(n)}_{(n+1)(n+1)} = y^{(n-1)}_{(n+1)(n+1)} - (y^{(n-1)}_{n\,(n+1)})^2 / y^{(n-1)}_{nn} \qquad (40)$$

For both $y^{(n)}_{(n+1)(n+1)}$ and $y^{(n-1)}_{nn}$ to become zero on the spinodal curve

$$\lim_{y^{(n)}_{(n+1)(n+1)} \to 0} [y^{(n-1)}_{(n)(n+1)}] = 0 \qquad (41)$$

Modell (1977) has suggested that when such problems occur, it is convenient to modify the stability criterion as

$$y^{(n)}_{(n+1)(n+1)}\, y^{(n-1)}_{nn} = 0 \qquad (42)$$

The only time this technique will fail is when $y^{(n-2)}_{(n-1)(n-1)}$ and even lower-order terms also become zero simultaneously. Modell (1977) then recommends that the product form of Equation (42) be enlarged until the indeterminancy is removed; that is

$$\prod_{j=n}^{i} y^{(j)}_{(j+1)(j+1)} = 0 \quad \text{for} \quad i = n-1, n-2, \ldots 1 \qquad (43)$$

There will always be one of these product terms which is not indeterminate since, if $i = 1$, then the product is simply given by $\mathcal{D}_{n+1}$, that is, the $(n + 1) - (n + 1)$ determinant where the rows and columns are second-order derivatives of $\underline{U}$ [see Equation (9), Beegle et al., 1974*b*].

Should the locus of $y^{(n-1)}_{nn} = 0$ become tangent at the critical point, then to remove the indeterminancy in $y^{(n)}_{(n+1)(n+1)(n+1)}$, multiply by $[y^{(n-1)}_{(n-1)(n-1)}]^3$. This results again from a step-down operation for third derivatives.

These techniques were, in fact, employed by Teja and Kropholler (1975) to obtain valid numerical values for critical points in the carbon dioxide-ethane system.

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NOTATION

$\underline{A}$ = total Helmholtz energy, A, molar Helmholtz energy
$\mathcal{D}_k$ = a k by k determinant in U_{ij}, $i, j = 1, \ldots k$
$\underline{G}$ = total Gibbs energy; G, molar Gibbs energy
$\underline{G}'$ = Legendre transform in the $(T, P, \mu_1, N_2, \ldots N_n)$ system
$\underline{G}^+$ = Legendre transform in the $(T, P, \eta_1, N_2, \ldots N)$ system
$\underline{H}$ = total enthalpy; H, molar enthalpy
$\mathcal{L}_i$ = determinant defined in Equation (14)
$\mathcal{M}_i$ = determinant defined in Equation (16)
n = number of components
N_j = moles of j; N, total moles
P = pressure
$\underline{S}$ = total entropy; S, molar entropy
T = temperature
$\underline{U}$ = total internal energy; U, molar internal energy
$\underline{V}$ = total volume; V, molar volume
x_i = independent, extensive, variable
$y^{(i)}$ = i^{th} Legendre transform
z_j = mole fraction of component j

Greek Letters

η_j = modified chemical potential of component j defined in Equation (31)
μ_j = chemical potential of component j
ξ_i = conjugate coordinate, intensive, variable to x_i, $\xi_i = (\partial y^{(0)}/\partial x_i)_{x[i]} = (\partial y^{(k)}/\partial x_i) \quad i > k$
ϕ_i = fugacity coefficient of component i

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Multivariable Computer Control of a Butane Hydrogenolysis Reactor:

Part I. State Space Reactor Modeling

A state space model is developed for an existing nonadiabatic packed-bed reactor which experiences axial and radial concentration and temperature gradients resulting from highly exothermic reactions involving several chemical species. The set of partial differential equations is reduced from three to two dimensions using orthogonal collocation. Further use of orthogonal collocation on the quasi steady state version of the differential equations results in a set of coupled algebraic and differential equations from which a linearized low-order state space model is obtained. The model parameters are estimated from reactor data, and the fitted model is used for design and implementation of a multivariable stochastic control schemes on the reactor. These applications are described in parts II and III of this paper.

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SCOPE

The catalytic chemical reactor represents one of the more complicated processes to model in chemical engineering. Because of this, it is essential when deriving a process model to keep in mind the purpose for which the model is to be used. If, for example, the model is to be used as the basis for on-line regulatory control of the reactor, large simplifications to most of the models proposed in the literature must be made. Although most of the models tend to be somewhat complex and, in general, unsuitable for control, by examining the formulation of these models some insight into the important effects occurring within a reactor may be gained, and ideas for simplifying the models for the purposes of control may be found.

Beek (1962) and Froment (1967, 1972) present great insight into the factors surrounding a complex model of a packed-bed reactor including estimation of transport properties and heat transfer effects. More recently, Froment (1974) reviews the current findings in the literature and comments on a number of still unanswered questions in the modeling of chemical reactors. Extensions to Beek's work are provided by Hlavcek (1970), particularly in the area of parameter estimation problems. Parametric sensitivity in fixed-bed reactors is discussed by Carberry and White (1969). Most of these studies address the problems appearing in single reaction systems of specific order under steady state conditions.

There are only a limited number of studies concerned with transient effects in packed tubular reactors. Most of these except Young and Finlayson (1973) appear to neglect radial gradients. Inclusion of both axial and radial gradients gives rise to a set of three-dimensional partial differential equations which presents a very difficult computational problem. Sinai and Foss (1970) consider an adiabatic reactor in which a non-catalyzed reaction occurs in the liquid phase of a solid liquid system. Crider and Foss (1966) attempt to isolate the important factors affecting