THE ISOTHERMAL FLASH PROBLEM. PART I. STABILITY

MICHAEL L. MICHELSEN

Instituttet for Kemiteknik, Danmarks Tekniske Højskole, Byning 229, 2800 Lyngby (Denmark)

(Received September 25th, 1981)

ABSTRACT

Michelsen, M.L., 1982. The isothermal flash problem. Part I. Stability. *Fluid Phase Equilibria,* 9: 1–19.

Stability analysis is suggested as a preliminary step in isothermal flash calculations, and a number of numerical methods for stability analysis based on Gibbs' tangent plane criterion are described. These methods, which are applicable for both single phase and multiphase systems, are developed mainly for Equation of State calculations using a single model for all fluid phases. Special adaptions ensuring convergence in critical regions are discussed.

INTRODUCTION

A severe problem associated with flash calculations at a given temperature and pressure using a single Equation of State is that the number of equilibrium phases is not known in advance. The conventional approach is to assume the number of phases present at equilibrium and to estimate initial values for the equilibrium factors. The material balance equations are solved for the phase fractions and the resulting phase compositions provide new values of the equilibrium factors. This procedure is repeated until convergence is obtained (Henley and Rosen, 1969; King, 1980). Various acceleration methods can be used to promote convergence (Boston and Britt, 1978; Mehra et al., 1980 a, b; Asselineau et al., 1979). Alternatively the equilibrium can be formulated as a Gibbs energy minimization problem (Gautam and Seider, 1979).

Both approaches can fail if the initial estimate of the iteration variables is too inaccurate, and both may require a substantial amount of computation only to arrive at a trivial solution in cases where the assumed number of phases is too high.

The present paper concerns numerical methods for deciding whether a phase is thermodynamically stable. The stability tests require no user-provided initial estimates of number of phases present at equilibrium or of the

equilibrium factors. The tests are all based on the tangent plane criterion of Gibbs, and for unstable systems they also provide the composition of a new phase which can be split off to decrease the Gibbs energy of the mixture. Hence an initial estimate for the subsequent flash calculation is also available. The test is applicable to single phase as well as to multiphase systems. The flash calculation will be discussed in a separate paper (Michelsen, 1981a).

THE TANGENT PLANE CRITERION

An extensive proof for the tangent plane criterion has very recently been presented (Baker et al., 1981) and only the parts of interest for the subsequent development will be given here.

We consider at given temperature and pressure (T_0, P_0) an M-component mixture with component mole fractions $(z_1, z_2, ..., z_M)$. The Gibbs energy of the mixture is

$$G_0 = \sum_i n_i \mu_i^0 \tag{1}$$

where μ_i^0 is the chemical potential of component i in the mixture.

Assume that this mixture is divided into two phases with mole numbers $N - \epsilon$ and ϵ, respectively, the amount ϵ of the second phase being infinitesimal. Let the mole fractions in phase II be $(y_1, y_2, ..., y_M)$.

The change in Gibbs energy is then

$$\Delta G = G_1 + G_{11} - G_0$$
$$= G(N - \epsilon) + G(\epsilon) - G_0 \tag{2}$$

A Taylor series expansion of G_1, discarding second order terms in ϵ, yields

$$G(N - \epsilon) = G(N) - \epsilon \sum_i y_i \left(\frac{\partial G}{\partial n_i} \right)_N = G_0 - \epsilon \sum_i y_i \mu_i^0 \tag{3}$$

or

$$\Delta G = G(\epsilon) - \epsilon \sum_i y_i \mu_i^0 = \epsilon \sum_i y_i \left(\mu_i(y) - \mu_i^0 \right) \tag{4}$$

Stability of the original mixture requires that its Gibbs energy is at the global minimum. Hence a necessary criterion for stability is that

$$F(y) = \sum_i y_i \left(\mu_i(y) - \mu_i^0 \right) \geq 0 \tag{5}$$

for all trial compositions y.

Geometrically $F(y)$ is the vertical distance from the tangent hyperplane to the Molar Gibbs energy surface at composition z to the energy surface at

composition y, as shown schematically in Fig. 1 for a binary mixture. Stability requires that the tangent hyperplane at no point lies above the energy surface.

For multiphase systems a necessary condition for equilibrium is that the individual species have identical chemical potentials in all phases.

It is easily shown that for a multiphase system satisfying the condition of equal potentials, the value of F does not depend on the phase investigated and eqn. (5) is also a sufficient condition for stability.

The total Gibbs energy of a J-phase system ($J \geqslant 1$) with $\mu_{ij} = \mu_i^{(1)}$ is

$$G^{(1)} = \sum_j \sum_i n_{ij}\mu_{ij} = \sum_i n_i \mu_i^{(1)} \tag{6}$$

A different phase split into L phases with mole fractions y_{il} and total phase mole numbers N_l has a Gibbs energy of

$$G^{(II)} = \sum_l \sum_i N_l y_{il} \mu_{il} \tag{7}$$

and the energy difference is

$$G^{(II)} - G^{(I)} = \sum_l \sum_i N_l y_{il} \mu_{il} - \sum_i n_i \mu_i^{(1)}$$

$$= \sum_l N_l \left(\sum_i y_{il} \left(\mu_{il} - \mu_i^{(1)} \right) \right) = \sum_l N_l F_l \tag{8}$$
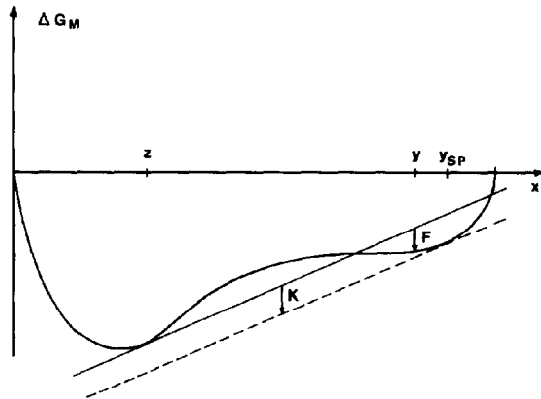

Fig. 1. Molar Gibbs' energy of mixing for binary mixture showing tangent at mole fraction z and tangent distance F at mole fraction y. Also shown is the parallel tangent at the stationary point.

since conservation of mass requires that $\sum_l N_l y_{il} = n_i$.

The energy change can only be negative provided at least one of the F_l is negative. Thus, the multiphase system is stable if eqn. (5) is satisfied.

Baker et al. state the tangent plane criterion eqn. (5) but give no numerical implementations. In this paper a variety of techniques for locating trial compositions y which indicate instability will be described.

IMPLEMENTATION OF CRITERION

Since all minima of $F(\mathbf{y})$ are located in the interior of the permissible region ($y_i \geqslant 0$, $\sum_i y_i = 1$), $F(\mathbf{y})$ will be non-negative if it is non-negative at all stationary points, that is, points where the derivatives with respect to all independent variables equal zero.

Straightforward differentiation with respect to the $M - 1$ independent mole fractions yields the stationarity condition

$$\mu_i(\mathbf{y}) - \mu_i^0 = K, \qquad i = 1, 2, \ldots, M \tag{9}$$

where K is independent of the component index i.

The corresponding stationary value is

$$F_{\mathrm{SP}} = \sum y_i K = K \tag{10}$$

that is, the system is stable provided K is non-negative at all stationary points. We notice that $\mathbf{y} = \mathbf{z}$ is a stationary point with the stationary value equal to zero.

At a stationary point the tangent hyperplane to the energy surface is parallel to the hyperplane at $\mathbf{z}$, K being the vertical distance between the planes, see Fig. 1.

For equations of state calculations it is more convenient to work in terms of fugacity coefficients. We obtain as our stability criterion

$$g(\mathbf{y}) = F(\mathbf{y})/RT_0 = \sum_i y_i(\ln y_i + \ln \phi_i - h_i) \geqslant 0 \tag{11}$$

where $\phi_i = \phi_i(\mathbf{y})$ and $h_i = \ln z_i + \ln \phi_i(\mathbf{z})$

The stationarity criterion is

$$\ln y_i + \ln \phi_i - h_i = k \qquad (i = 1, 2, \ldots, M) \tag{12}$$

Introducing new variables $Y_i = \exp(-k) y_i$ we obtain

$$\ln Y_i + \ln \phi_i - h_i = 0 \qquad (i = 1, 2, \ldots, M) \tag{13}$$

The new independent variables Y_i can formally be interpreted as mole numbers, the corresponding mole fractions being $y_i = Y_i/\sum_j Y_j$. Stationary points are located as solutions to eqn. (13), and stability is verified provided at all stationary points $k \geqslant 0$, corresponding to $\sum_i Y_i \leqslant 1$.

Conversely, we know that a phase is unstable if we can locate a stationary point where $\Sigma_i Y_i > 1$, and we also know that a split of the original phase in two phases with mole fractions y_i in the second phase will decrease the total Gibbs energy if the amount of the second phase is chosen small enough.

We can formulate a different but equivalent criterion based on the variables Y_i

$$g^*(\mathbf{Y}) = 1 + \sum_i Y_i (\ln Y_i + \ln \phi_i - h_i - 1) \geqslant 0 \tag{14}$$

No constraints on the Y_i except $Y_i > 0$ are required. The equivalence is seen as follows:

Stationarity of g^* requires

$$\partial g^* / \partial Y_i = 0 \qquad (i = 1, 2, ..., M) \tag{15}$$

yielding

$$\ln Y_i + \ln \phi_i - h_i = 0 \qquad (i = 1, 2, ..., M) \tag{16}$$

that is, the stationary points of g^* correspond to those of g.

In addition

$$g^*_{SP} = 1 - \sum_i Y_i = 1 - \exp(-k) = 1 - \exp(-g_{SP}) \tag{17}$$

which shows that the stationary values of g and g^* are of equal sign.

Finally,

$$g^*(\mathbf{Y}) = \theta g(\mathbf{y}) + (1 - \theta + \theta \ln \theta) \tag{18}$$

where $\theta = \Sigma_i Y_i$.

Since the second term is always non-negative g will be negative at all points where g^* is negative; thus a negative g^* shows that the system is unstable.

SOLUTION METHODS

Direct substitution or accelerated direct substitution are obvious candidates for solving the stationarity condition eqn. (16). Subsequent iterates are simply determined from

$$\ln Y_i^{(t+1)} = h_i - \ln \phi_i^{(t)} \tag{19}$$

In Appendix A is shown that direct substitution converges to a *local* minimum of g^*. If the composition dependence of the fugacity coefficients is weak convergence will be rapid.

Direct substitution has linear convergence with a rate determined by the magnitude of the eigenvalues of the partial derivatives matrix $\mathbf{S}$, taken at the

solution $Y^{(\infty)}$

$$S_{ij} = \left(\frac{\partial \ln Y_i^{(t+1)}}{\partial \ln Y_j^{(t)}} \right)_{t=\infty} = - Y_j \left(\frac{\partial \ln \phi_i}{\partial Y_j} \right)_{Y^{(\infty)}} \tag{20}$$

The asymptotic rate is given by

$$e^{(t+1)} = |\lambda|_{max}\, e^{(t)} \tag{21}$$

where e is the norm of the error vector,

$$e^{(t)} = \sum_i \left(\ln Y_i^{(t)} - \ln Y_i^{(\infty)} \right)^2 \tag{22}$$

For an unstable system all eigenvalues corresponding to the desired global minimum will be smaller than one, but exactly one eigenvalue will approach one at the critical point. In contrast, when a phase split calculation using direct substitution is performed, two eigenvalues approach 1 at the critical point (Michelsen, 1981a). Furthermore, for many Equations of State, only a few eigenvalues will differ significantly from zero. One may for example show, proceeding as in Michelsen and Heidemann, 1981, for critical point calculations, that the SRK-equation (Soave, 1972), which is used for all examples in this work, and the Peng–Robinson equation (Peng and Robinson, 1976) only have two non-zero eigenvalues of S for systems where all binary interaction coefficients are zero. Since these coefficients are usually small we may expect that only two eigenvalues of S differ significantly from
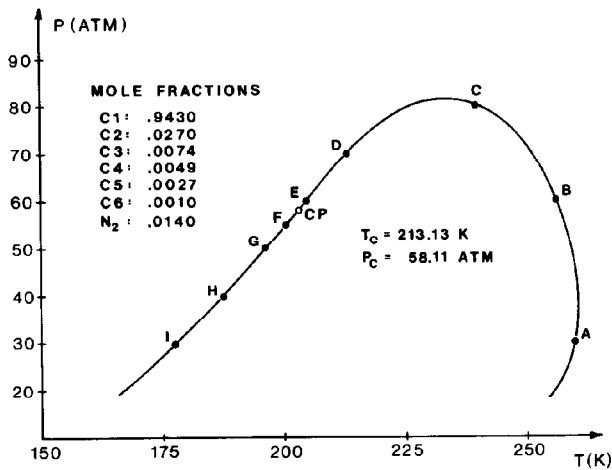

Fig. 2. Phase envelope for a seven-component mixture, calculated from the SRK-equation.

zero. The error vector in subsequent iterations is then quickly confined to the subspace spanned by the corresponding eigenvectors, and we can expect acceleration methods such as the General Dominant Eigenvalue Method (Crowe and Nishio, 1975) using one or two terms, or Broydens method (Dennis and Moré, 1977), to be quite efficient.

A minimization method could also be used. Since evaluation of the partial composition derivatives of the fugacity coefficients is normally fairly inexpensive (Michelsen, 1981b) the second order method of Murray (Murray, 1972) is attractive and of more general applicability since its performance does not depend on the rank of **S**.

A phase envelope for a typical natural gas mixture containing 7 components is shown on Fig. 2. The non-trivial solution to eqn. (16) was found for a number of points on the phase boundary, and the eigenvalues of **S** were calculated.

In Table 1 are listed the three largest eigenvalues at each point. Even in the critical region only two differ significantly from zero and in effect only one is of any real importance.

When direct substitution is used the approach to the solution will be in the direction of the eigenvector corresponding to the dominant eigenvalue of **S**. This can be used to terminate iterations early in cases where the trivial solution $Y = z$ is approached, as shown in Appendix B.

At each point is calculated

$$\beta = \Sigma(Y_i - z_i)\frac{\partial g^*}{\partial Y_i} \tag{23}$$

TABLE 1

The 3 largest eigenvalues of matrix **S** at the nontrivial solution of eqn. (16)

Point	Temperature	Pressure (atm)	Eigenvalues of **S**		
			λ_1	λ_2	λ_3
A	259.6	30	0.095	1.8×10^{-4}	-1.3×10^{-4}
B	256.2	60	0.252	-2.9×10^{-4}	1.9×10^{-4}
C	239.5	80	0.506	-6.0×10^{-4}	2.1×10^{-4}
D	212.93	70	0.874	-1.3×10^{-3}	2.5×10^{-4}
E	204.65	60	0.994	-1.5×10^{-3}	1.6×10^{-4}
F	200.73	55.2	0.933	-1.2×10^{-3}	5.0×10^{-5}
G	196.35	50	0.452	-1.0×10^{-3}	~ 0
H	187.6	40	0.076	-6.8×10^{-4}	~ 0
I	177.7	30	0.025	-3.5×10^{-4}	~ 0

8

and the ratio

$$r = 2g^*/\beta \tag{24}$$

which will approach one when $\mathbf{Y}$ approaches a trivial solution.

If subsequent iterates lead to increasing values of r it is unlikely that a minimum is located between $\mathbf{Y}$ and $\mathbf{z}$. In such cases we abandon the search when r exceeds 0.8.

A computationally more efficient form is obtained by substituting as iteration variables $\alpha_i = 2\sqrt{Y_i}$. In terms of these we obtain

$$q_i = \frac{\partial g^*}{\partial \alpha_i} = \sqrt{Y_i}(\ln Y_i + \ln \phi_i - h_i) \tag{25}$$

and

$$A_{ij} = \frac{\partial^2 g^*}{\partial \alpha_i \partial \alpha_j} = B_{ij} + \tfrac{1}{2}\delta_{ij}(\ln Y_i + \ln \phi_i - h_i) \tag{26}$$

with

$$B_{ij} = \delta_{ij} + (Y_i Y_j)^{1/2}\frac{\partial \ln \phi_i}{\partial Y_j} \tag{27}$$

At the solution the second term in eqn. (26) is zero. In addition the first term equals the identity matrix for an ideal mixture and the additional term $(Y_i Y_j)^{1/2}$ $(\partial \ln \phi_i/\partial Y_j)$ is of low effective rank for nonideal mixtures. Consequently we may expect a quasi-Newton minimization procedure to be efficient.

We suggest that the double rank BFGS-update for the inverse Hessian (Dennis and Moré, 1977, p. 72) is used with the identity matrix as our initial approximation. This update has the property of hereditary positive definiteness, and convergence will be to a local minimum.

In practice there is little difference between the number of iterations required using continued updating and the number needed when the inverse Hessian is reset to the identity matrix after each iteration. The latter approach is therefore recommended since it only requires storage of the vectors from the last iteration and only uses scalar vector products.

Finally, the trivial solution is a local minimum provided $\mathbf{B}$ is positive definite at $\mathbf{Y} = \mathbf{z}$. Positive definiteness of $\mathbf{B}$ or of an equivalent matrix involving the same partial composition derivatives is the (necessary) stability criterion normally found in the literature. The locus of points in the P–T plane where $\mathbf{B}$ has a zero eigenvalue is called the limit of intrinsic stability (Modell and Reid, 1974), and the region where the phase is unstable but $\mathbf{B}$ positive definite is the metastable region. In Fig. 3 is shown the stability limit for the mixture given in Fig. 2. We notice that the criterion of positive
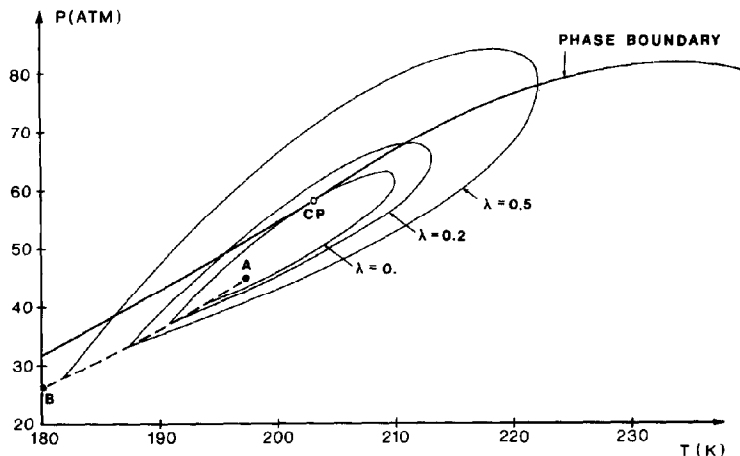
Fig. 3. Stability limit and contours of constant λ_{min} for mixture of Fig. 2. On the line A–B two roots of the compressibility factor equation yield equal Gibbs energies.

definiteness only covers a small but important region close to the critical point.

The scaling used for the matrix **B** is very convenient since the magnitude of the smallest eigenvalue for a positive definite **B** provides a measure of the distance from the stability limit, the value ranging from zero at the stability limit to one for an ideal gas. Contours for $\lambda_{min} = 0.2$ and $\lambda_{min} = 0.5$ are shown in Fig. 3.

SELECTING INITIAL ESTIMATES

Except in the case where the trivial solution **Y** = **z** is the only minimum of g^* the minimization problem has multiple solutions. If **B** has a negative eigenvalue at least two negative minima of g^* will exist. In the remaining part of the two-phase region the trivial solution is a minimum and in addition at least one negative minimum exists. In the one-phase region a positive minimum may exist in addition to the trivial solution.

To insure that negative minima are detected it is necessary to use multiple initial estimates. For vapour–liquid equilibrium problems these estimates are selected as follows:

At low pressures K-factors in hydrocarbon systems are reasonably well approximated by

$$K_i = \frac{P_{c_i}}{P} \exp\left\{5.42\left(1 - \frac{T_{c_i}}{T}\right)\right\} \tag{28}$$

The objective function $g^*(Y)$ is minimized using the following two sets of initial estimates:

$$Y_i = K_i z_i \qquad (29a)$$

and

$$Y_i = z_i/K_i \qquad (29b)$$

Normally one of these initial estimates will converge to the trivial solution and the other to the desired minimum for a specification in the two phase region. In many cases only a single set of estimates is required, e.g. when the phase investigated is clearly liquid-like or clearly vapour-like, in which case only (29a) or (29b), respectively, are used. In the critical region, however, we do not know in advance whether our trial composition should be lighter than or heavier than the phase investigated, and both are required.

In case the compressibility factor equation has multiple roots the root corresponding to the state with the lower Gibbs energy is selected.

In Table 2 is shown the number of iterations required to determine the minimum of g^* using eqns. (29a) and (29b) as initial estimates for the mixture given in Fig. 2 at various temperatures and pressures. The points are selected just within the phase boundary. The convergence criteria used were

$$\sum_i (\Delta \alpha_i)^2 < 10^{-10} \qquad (30)$$

for a nontrivial solution, and

$$g^* < 10^{-3}, |r - 1| < 0.2 \qquad (31)$$

for an approach to the trivial solution.

The initial estimate is not critical, and essentially it is only required that the two Y-vectors are located on opposite sides of the phase composition z. This is illustrated for the 3-component system shown in Fig. 4. This mixture is capable of splitting into 3 phases, but here we only consider points along the two-phase boundary. The correct solution is found without problems

TABLE 2

Number of iterations required to converge initial estimates (29a, b). The * indicates convergence to the trivial solution

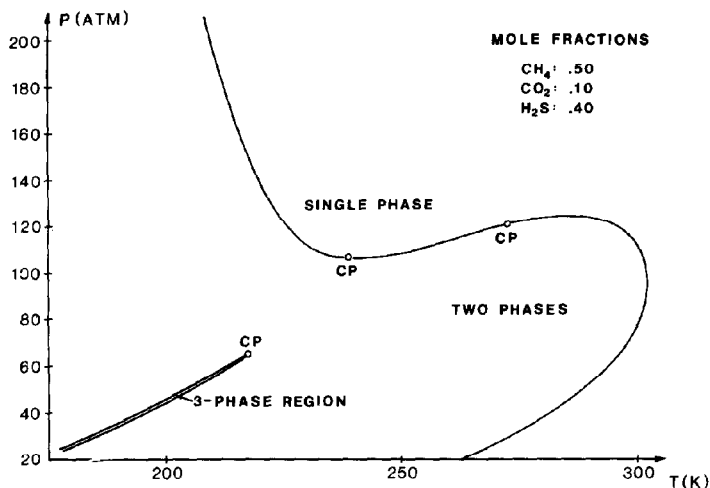| Point	A	B	C	D	E	F	G	H	I
29(a)	1*	1*	1*	2*	6*	5	5	4	4
29(b)	3	4	6	9	15	9*	6*	4*	3*

Fig. 4. Phase diagram for a ternary mixture capable of splitting into 3 phases. (SRK-equation.)

between the two critical points and on the high pressure branch, where eqns. (29a,b) are very inaccurate estimates of the equilibrium factors.

When the stability of multiphase systems is investigated, different initiation procedures are required, since the number of trivial solutions equals the number of phases already present. Most frequently the search is for an additional liquid phase, and general approximative K-factors of the eqn. (28) type are not available for liquid–liquid equilibrium.

We suggest the following procedure:

A number of initial estimates corresponding to the number of components in the system is chosen, and a pure phase is selected as the initial phase composition. For the hydrocarbons, however, only the lightest and the heaviest components are tried. Two additional estimates are used, namely (a) $Y_i = \exp(h_i)$ corresponding to a hypothetical ideal gas (ln $\phi_i = 0$) and (b) the Y_i are selected as the arithmetic mean of the phase compositions already present.

A slight modification is needed for supercritical or nearly supercritical components, where the pure phase is not a liquid under the specified conditions. As a simple example we can consider a mixture of 50% methane and 50% hydrogen sulphide at 190 K, 40 atm. The Gibbs energy of mixing for this binary system is shown in Fig. 5a. The stability analysis will readily find that the Gibbs energy can be decreased by forming a vapour phase, and a subsequent phase split calculation will yield two phases containing 2%
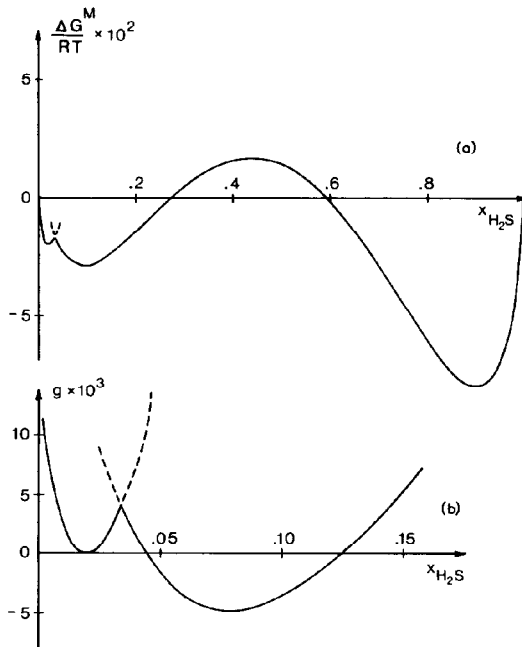
Fig. 5. Molar Gibbs energy of mixing for a binary mixture of hydrogen sulphide and methane at 190 K, 40 atm (a), and tangent plane distance at 2% hydrogen sulphide (b).

hydrogen sulphide and 89% hydrogen sulphide, respectively. A plot of the tangent plane distance vs. trial phase composition for the two phase mixture (Fig. 5b) reveals that this solution is not stable since a negative minimum is found at about 8% hydrogen sulphide. The equilibrium state is two liquid phases containing about 8% hydrogen sulphide and about 89% hydrogen sulphide, respectively. The methane rich minimum is, however, difficult to detect since using pure methane as the initial estimate leads to the trivial solution at 2% hydrogen sulphide.

For this reason the state of the trial phase is chosen as liquid, provided a liquid state exists, for all initial estimates starting with a pure phase. If a liquid state does not exist, the pure-phase fugacity coefficients can be evaluated at a lower temperature or a higher pressure to ensure liquid-like conditions. Subsequent iterations are performed at the correct temperature and pressure, but with selection of the liquid-like root of the compressibility factor equation regardless of the Gibbs energy. For the additional initial estimate corresponding to an ideal vapour phase we select the vapour-like

root, and in practice the use of this additional estimate makes it very unlikely that a vapour solution is missed.

Rather than converging each initial estimate in turn, calculations are done in parallel for all estimates, and only a limited number of iteration steps are performed. For each trial phase the value of r corresponding to the closest phase composition is evaluated, and iterations are discontinued when r is increasing, or when g^* is small and r close to one. If no negative g^* are encountered after 4 iterations the Y-vector with the smallest value of r is converged using the Murray method. If this leads to a trivial solution we assume that the system is stable.

This procedure does not guarantee the detection of all negative minima, but in practice it has turned out to be very reliable at a reasonable computational cost. Numerous modifications are evidently possible. Starting with pure trial phases has the advantage that component fugacity coefficients are evaluated cheaply and that, for example, liquid immiscibility in highly immiscible systems is immediately detected. The Quasi-Newton minimization procedure could be used without adding seriously to the storage requirements since the BFGS update only requires storage of the vectors from the previous step.

ALTERNATIVE METHODS FOR LOCATING THE MINIMA

The methods described in the previous section are most likely to fail in finding the minimum for a phase when it is nearly critical, that is, in cases where the desired minimum is located close to a trivial solution.

Two methods which are complementary to the one previously described, in the sense that they perform particularly well in such situations, are next described.

The first of these methods can be regarded as an extension of the positive definiteness criterion. Provided $\mathbf{B}$ is positive definite it is usually concluded that this criterion gives no information. However, if the smallest eigenvalue of $\mathbf{B}$ is close to zero the increase in g^* along the eigenvector corresponding to this eigenvalue will be much smaller than the increase in orthogonal directions, and higher order effects might well make g^* negative close to the point of origin. We therefore propose a one-dimensional search of $g^*(d)$ with

$$\alpha_i = 2\sqrt{z_i} + d \cdot u_i \tag{32}$$

where

$$\mathbf{B}\mathbf{u} = \lambda_{min}\mathbf{u}, \quad \mathbf{u}^T\mathbf{u} = 1 \tag{33}$$

To avoid negative α_i we select

$$\alpha_i = 2\sqrt{z_i} \bigg/ \left\{ 1 - d\frac{u_i}{2\sqrt{z_i}} \right\} \tag{34}$$

14

for elements with negative u_i.

A Taylor series expansion of $g*$ from $d = 0$ yields

$$g*(d) = \tfrac{1}{2}\lambda_{min}d^2 + \tfrac{1}{6}(g*)^{(3)}(0)\,d^3 + \mathcal{O}(d^4) \tag{35}$$

indicating that the direction of search should be selected in accordance with the sign of the third derivative of $g*$, which is easily evaluated numerically.

We intend to trace the valley originating from point z in the u direction. This valley leads initially in the direction of the eigenvector, and the gradient q is parallel to u. At larger d, the points calculated from eqns. (32–34) will no longer be located in the bottom of the valley, due to the slight curvature of the valley, and we observe that q is no longer parallel to u. A reduction in $g*$ can then be obtained by an adjustment step in a direction orthogonal to u, chosen such that the components of q which are orthogonal to u are removed.

At point d we evaluate α (from 32–34) and $q(\alpha)$. The correction step is found from

$$B\Delta\alpha = -\left(q - \left(u^T q\right) u\right) \tag{36}$$

and the corrected value $g*(\alpha + \Delta\alpha)$ is evaluated. An actual calculation is not required since $g*$ can be approximated using a second order expansion from α.

$$g*(\alpha + \Delta\alpha) = g*(\alpha) + \Delta\alpha^T q + \tfrac{1}{2}\Delta\alpha^T B\Delta\alpha \tag{37}$$

The eigenvector–eigenvalue pair (u, λ_{min}) are determined readily by inverse iteration (Wilkinson, 1965). B is then available in factorized form,
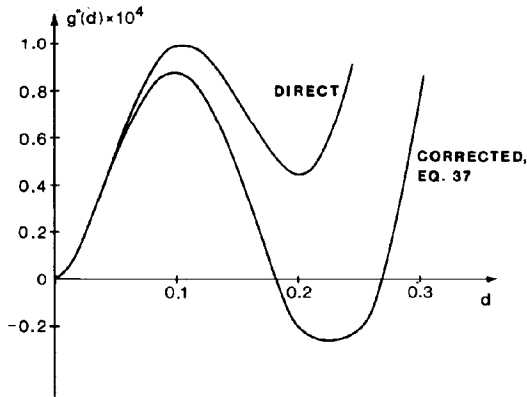

Fig. 6. Tangent plane distance along eigenvector for smallest eigenvalue for mixture of Fig. 2 at 199 K, 53.12 atm.

TABLE 3

Values of g^* calculated along eigenvector corresponding to smallest eigenvalue. Mixture of Fig. 2, $T = 199.0$ K, $P = 53.12$ atm

d	$g^*(\alpha)$ $(\times 10^{-5})$	$g^*(\alpha + \Delta\alpha)$ Correct $(\times 10^{-5})$	$g^*(\alpha + \Delta\alpha)$ $(\times 10^{-5})$ Approx. from eqn. (37)
0.1	9.79	8.74	8.75
0.2	4.47	−2.16	−2.17
0.22	5.35	−3.54	−3.53
0.24	8.37	−3.42	−3.36
0.26	13.9	−1.57	−1.41

and the computational load associated with the evaluation of $\Delta\alpha$ is negligible.

In Fig. 6 is shown $g(d)$ for a point just inside the phase boundary with $\lambda_{min} = 0.077$. Table 3 gives representative values of $g^*(\alpha)$, $g^*(\alpha + \Delta\alpha)$ and $g^*(\alpha + \Delta\alpha)$ calculated from eqn. (37).

In case the line search yields a minimum with a small positive value the corresponding phase composition is used as the initial estimate for location of the exact minimum in all variables. Normally this minimum will be very close to the line.

USING VOLUME AS A PARAMETER

All previous stability investigations have been performed at constant temperature and pressure using the Gibbs energy as a criterion. An equivalent criterion can be formulated in terms of the Helmholtz energy, yielding (Heidemann, 1980)

$$h(\mathbf{y},v) = \sum_i y_i(\mu_i(\mathbf{y},v) - \mu_i(\mathbf{z},v_0)) - v(P(v,\mathbf{y}) - P_0) \geqslant 0 \qquad (38)$$

with stationarity conditions

$$\mu_i(\mathbf{y},v) - \mu_i(\mathbf{z},v_0) = K \qquad (39)$$

$$P(v,\mathbf{y}) - P_0 = 0 \qquad (40)$$

In these equations v is the molar volume of the trial phase and v_0 is the molar volume of the phase investigated at the given pressure P_0.

Heidemann suggested that the family of solutions to eqn. (39) was evaluated, disregarding for the moment the equality of pressure condition,

eqn. (40). The entire family of solutions can be constructed, using the trivial solution $y = z$, $v = v_0$ as the starting point, by an extrapolation technique as described by Michelsen, 1980. Points where eqn. (40) is also satisfied represent the desired stationary points.

The procedure is characterized by a high degree of safety, but unfortunately it is not competitive in speed with the methods suggested earlier. The procedure is particularly useful for checking results using the Gibbs energy criterion since it enables one to detect whether all relevant minima have been found.

CONCLUSIONS AND EXTENSIONS

A variety of computational techniques for resolving the single phase stability problem at given temperature and pressure have been developed. It is suggested that such procedures should be used as a preliminary step in flash calculations, since a favourable initial estimate of the phase compositions is also provided.

The extension to isenthalpic and isentropic flash problems is straightforward. Given for example the pressure and the enthalpy a temperature matching these specifications is determined, and the stability check can be performed at the resulting (T, P).

Chemically reacting systems at given T and P can also be handled by an initial calculation of the extent of reactions which minimizes the single phase Gibbs energy of the system. The stability criterion is then applicable to the chemically equilibrated phase.

With the exception of the method using volume as a parameter all techniques can be applied in calculations with split models provided a proper normalization of the chemical potentials is used.

ACKNOWLEDGEMENTS

APPENDIX A: CONVERGENCE OF DIRECT SUBSTITUTION

Direct substitution will converge to a solution where the magnitude of the numerically largest eigenvalue of the matrix S (eqn. 20) is smaller than one. Eigenvalues of S satisfy

$$Sx = \lambda x \tag{A1}$$

or

$$-\phi \mathbf{D} \mathbf{x} = \lambda \mathbf{x} \tag{A2}$$

with

$$\Phi_{ij} = \frac{\partial \ln \phi_i}{\partial Y_j} \text{ and } D_{ij} = \delta_{ij} Y_i$$

eqn. (A2) can be rewritten

$$\mathbf{D}^{1/2} \phi \mathbf{D}^{1/2} \mathbf{v} = -\lambda \mathbf{v} \tag{A3}$$

with $\mathbf{v} = \mathbf{D}^{1/2} \mathbf{x}$

or $\left\{ \mathbf{I} + \mathbf{D}^{1/2} \phi \mathbf{D}^{1/2} \right\} \mathbf{v} = (1 - \lambda) \mathbf{v} \tag{A4}$

The matrix $\mathbf{I} + \mathbf{D}^{1/2} \phi \mathbf{D}^{1/2}$ equals the matrix $\mathbf{B}$ of eqn. 27, which is the Hessian Matrix of g^* with respect to the scaled variables $\alpha_i = 2/\overline{Y}_i$, that is

$$\mathbf{B} \mathbf{v} = (1 - \lambda) \mathbf{v} \tag{A5}$$

or

$$\lambda_B = 1 - \lambda_S$$

Since convergence of the direct substitution requires that $|\lambda_S| < 1$ all eigenvalues of $\mathbf{B}$ will be positive at the solution and hence the condition for the solution being a local minimum of g^* is satisfied.

APPENDIX B: APPROACH TO THE TRIVIAL SOLUTION

At a stage where subsequent iterates are confined essentially to a line connecting our trial point $\mathbf{Y}$ and the trivial solution $\mathbf{z}$, we can consider g^* in dependence of a distance parameter s along this line,

$$g^*(s) = g^*(\mathbf{z} + s(\mathbf{Y} - \mathbf{z})) \tag{B1}$$

From the definition of g^*,

$$g^*(0) = \left(\frac{\mathrm{d} g^*}{\mathrm{d} s} \right)_{s=0} = 0 \tag{B2}$$

while at $s = 1$

$$g^*(1) = g^*(\mathbf{Y}), \quad \beta = \left(\frac{\mathrm{d} g^*}{\mathrm{d} s} \right)_{s=1} = \sum_i (Y_i - z_i) \left(\frac{\partial g^*}{\partial Y_i} \right) \tag{B3}$$

If $\mathbf{Y}$ is close to $\mathbf{z}$ and no minima are located between $\mathbf{Y}$ and $\mathbf{z}$ we can to a first approximation assume that the gradient $\mathrm{d}g/\mathrm{d}s$ is linear in s:

$$\mathrm{d} g^*/\mathrm{d} s = \beta s \tag{B4}$$

which implies

$$g^*(s) = \tfrac{1}{2}\beta s^2 \tag{B5}$$

This indicates that the ratio $r = 2g^*/\beta$ will approach unity as Y gets closer to z, provided no minima are located between the two points.

LIST OF SYMBOLS

A	Hessian matrix, eqn. 26
B	matrix of derivatives, eqn. 27
d	distance parameter
e	error norm, eqn. 21
F	tangent plane distance
g, g^*	objective functions
G	Gibbs energy
h_i	$\ln z_i + \ln \phi_i(\mathbf{z})$
i, j	component index
k	dimensionless chemical potential difference
K	chemical potential difference
l	phase index
n_i	component mole number
N_l	phase mole number
P, P_0	pressure
P_c	critical pressure
$\mathbf{q}$	gradient vector
r	gradient ratio, eqn. 24
S	matrix of second derivatives
t	iteration number
T, T_0	temperature
T_c	critical temperature
$\mathbf{u}$	eigenvector of B, eqn. 33
v, v_0	molar volume
$\mathbf{y}$	mole fraction vector, trial phase
$\mathbf{Y}$	mole number vector
$\mathbf{z}$	mole fraction vector, phase investigated
α	vector of independent variables, $\alpha_i = 2\sqrt{Y_i}$
β	gradient eqn. 23
δ_{ij}	Kronecker delta, $\delta_{ii} = 1$, $\delta_{ij} = 0, j \neq i$
ϵ	moles of trial phase
λ	eigenvalue
ϕ_i	fugacity coefficient of component i
θ	$\Sigma_i Y_i$

REFERENCES

Asselineau, L., Bogdanic, G. and Vidal, J., 1979. A versatile algorithm for calculating vapour–liquid equilibria. Fluid Phase Equilibria, 3: 273–290.

Baker, L.E., Pierce, A.C. and Luks, K.D., 1981. Gibbs energy analysis of phase equilibria. SPE/DOE Second Joint Symposium on Enhanced Oil Recovery, Tulsa, Oklahoma.

Boston, J.F. and Britt, H.I., 1978. A radically different formulation and solution of the single stage flash problem. Comput. Chem. Eng., 2: 109–122.

Crowe, A.M. and Nishio, M., 1975. Convergence promotion in the simulation of chemical processes — The general dominant eigenvalue method. AIChE J., 21: 528–533.

Dennis, J.E. and Moré, J.J., 1977. Quasi-Newton methods, motivation and theory. Siam Rev., 19: 46–89.

Gautam, R. and Seider, W.D., 1979. Computation of phase and chemical equilibrium. AIChE J., 25: 991–1015.

Heidemann, R.A., 1980. Private communication.

Henley, E.J. and Rosen, E.M., 1969. Material and energy balance computation. John Wiley, New York.

King, C.J., 1980. Separation Processes. McGraw-Hill.

Mehra, R.K., Heidemann, R.A. and Aziz, K., 1980a. Acceleration of the direct substitution method of vapour–liquid equilibrium calculations, Paper Presented at 30th Canadian Chemical Engin. Conf., Edmonton.

Mehra, R.K., Heidemann, R.A. and Aziz, K., 1980b. Computation of multiphase equilibria for compositional simulators, SPE 9232, Paper presented at 55 Annual Fall Technical Conference and Exhibition, SPE, Dallas, Texas.

Michelsen, M.L., 1980. Calculation of phase envelopes and critical points for multicomponent mixtures. Fluid Phase Equilibria, 4: 1–10.

Michelsen, M.L. and Heidemann, R.A., 1981. Calculation of critical points from cubic two-constant equations of state. AIChE J., 27: 521–523.

Michelsen, M.L., 1981a. The isothermal flash problem. Part II: Phase split calculation. Fluid Phase Equilibria, 8: 00–00.

Michelsen, M.L., 1981b. Partial derivatives of thermodynamic properties from equations of state. SEP 8109, Instituttet for Kemiteknik.

Modell, M. and Reid, R.C., 1974. Thermodynamics and its applications. Prentice Hall, Englewood Cliffs, N.J.

Murray, W., 1972. Second derivative methods, in W. Murray (Ed.), Methods for unconstrained optimization. Academic Press, London.

Peng, D.Y. and Robinson, D.B., 1976. A new two constant equation of states. Ind. Eng. Chem. Fundam., 15: 59–64.

Soave, G., 1972. Equilibrium constants from a modified Redlich–Kwong equation of state. Chem. Eng. Sci., 27: 1197–1203.

Wilkinson, J.H., 1965. The Algebraic Eigenvalue Problem, Chap. IX. Clarendon Press, Oxford.