

PHASE EQUILIBRIUM CALCULATIONS. WHAT IS EASY AND WHAT IS DIFFICULT?

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Abstract—Calculation of phase equilibrium for a mixture of given composition requires specification of two process variables, typically chosen from among the following: temperature, pressure, vapour fraction, enthalpy, entropy or volume. The difficulties associated with solving the equilibrium equations are strongly related to the chosen selection of these process variables. The aim of the present paper is to outline the characteristics associated with the different types of specification in order to provide guidelines for efficient and robust solution algorithms.

INTRODUCTION

Calculation of phase equilibrium is an essential and recurrent element in the simulation of chemical processes, and algorithms for phase equilibrium calculation are therefore required to be robust as well as efficient. Important applications requiring such calculations comprise single-stage processes, i.e. flash and saturation point calculations, as well as multi-stage processes such as distillation, adsorption and extraction. In the simulation of multistage processes the phase equilibrium calculation is tightly coupled with the interstage material balances, and efficient procedures for simulation of multistage units are therefore based on simultaneous solution of the material- and energy-balances and the equilibrium relations. In the present work we only consider single-state equilibrium calculations, with particular emphasis on the demands to the solution procedure imposed by different specifications for the equilibrium calculation and by different types of thermodynamic models.

BASIC EQUATIONS OF PHASE EQUILIBRIUM

We consider 1 mole of a C -component mixture of overall composition z separating into two phases, a liquid phase of composition x and a vapour phase of composition y , the equilibrium temperature and pressure being (T, P) . The vapour fraction, i.e. the amount of vapour formed per mole of feed, is denoted β .

It is further assumed that thermodynamically consistent models are available for calculation of liquid and vapour phase properties, and that all properties (i.e. fugacity coefficients, density and enthalpy) for a

given phase are calculated by means of the same thermodynamic model. Frequently, the same thermodynamic model, e.g. an equation of state, is used for the calculation of the properties of both phases, but is it also possible to use a hybrid approach with different models for the liquid and vapour phases, e.g. an activity coefficient model combined with a pure component fugacity expression for the liquid phase and an equation of state for the vapour.

The following set of equations apply to any two-phase equilibrium:

C material balance equations:

$$(1 - \beta)x_i + \beta y_i - z_i = 0, \quad (1)$$

C equilibrium relations:

$$f_i^l(T, P, x) - f_i^v(T, P, y) = 0, \quad (2)$$

1 summation of mole fractions relation:

$$\sum_{i=1}^C (y_i - x_i) = 0, \quad (3)$$

i.e. a total of $(2C + 1)$ equations relating the $2C + 3$ variables, (T, P, β, x, y) . To complete the definition of the desired problem, two additional specifications are required. These can be written in the general form:

$$S_1(T, P, \beta, x, y) = 0, \quad (4)$$

$$S_2(T, P, \beta, x, y) = 0. \quad (5)$$

In their simplest form, these specification equations merely assign values to two of the independent variables, e.g.

$$S_1 = P - P_{\text{spec}}, \quad S_2 = \beta - \beta_{\text{spec}},$$

but the specification equations could also typically involve properties like the total volume V , entropy S or enthalpy H of the equilibrium mixture, e.g. for the isenthalpic flash:

$$S_1 = P - P_{\text{spec}},$$

$$S_2 = (1 - \beta)h_1(T, P, x) + \beta h_v(T, P, y) - H_{\text{spec}}.$$

UNIQUENESS OF SOLUTION; THE TRIVIAL SOLUTION

A factor of crucial importance for the solution algorithm is whether a given specification corresponds to a unique solution. When different thermodynamic models are used for the liquid and vapour phases, uniqueness is expected, except in rare cases such as bubble point temperature calculations for mixtures containing solutes that exhibit a temperature maximum in Henry's law constant. Unfortunately, nonuniqueness, as well as "false solutions" is a severe problem when the same model is used for both phases. In particular, the so-called "trivial solution" has to be taken into account. The trivial solution $x = y = z$ satisfies equations (1–3) at all (T, P) , for which the equation of state

$$P = P(z, T, v), \quad (6)$$

has only one root for the molar volume v , leading to identical values of liquid and vapour phase properties.

For some specifications, the trivial solution is the only solution to the phase equilibrium calculation, whereas in other situations the trivial solution should be considered a "false" or undesired solution as valid, nontrivial solutions also exist.

An additional complication with the equation of state based calculations is the existence of a "critical region" near the mixture critical point, characterized by equilibrium phases of nearly identical composition. The phase equilibrium equations are frequently difficult to converge in the critical region, and inappropriate initial estimates or lack of precaution in the iterative procedure is particularly likely to lead to the trivial solution for calculations with solution in the critical region.

VERIFICATION OF THE SOLUTION

Satisfaction of the set of equations (1–3) with the associated specifications (4, 5) is only a necessary condition for phase equilibrium. An additional requirement is that the mixture must be thermodynamically stable, which requires that the mixture Gibbs energy at the current (T, P) is at its global minimum. Equality of fugacities is obviously a prerequisite for minimal G , and an additional

requirement is that the matrix of second derivatives of G with respect to the independent composition variables is positive definite, the well known condition of intrinsic stability.

Verification of a global minimum in G can be performed by means of the tangent plane condition (Baker *et al.*, 1982; Michelsen, 1982a). An equilibrium state with $f_i^l = f_i^v = f_i^*$ is stable provided the condition:

$$\sum_{i=1}^C W_i [\ln f_i(w) - \ln f_i^*] \geq 0, \quad (7)$$

for any trial phase composition w . Satisfaction of the tangent plane condition is a *necessary and sufficient* condition for stable equilibrium, i.e. for a global minimum in G . If we are able to locate a composition violating equation (7), formation of a new phase of this composition in a small amount leads to reduction of the mixture Gibbs energy.

Geometrically, the left-hand side of equation (7) represents the vertical distance from the tangent plane to the (reduced) Gibbs energy surface at the postulated equilibrium composition to the surface itself at composition w , as illustrated in Fig. 1 for a binary mixture. It is observed that the tangent plane distance for the mixture of Fig. 1 is negative for trial phase compositions in the range $0.12 < w_1 < 0.40$.

Stability of the mixture with composition z does thus require that the tangent plane to the Gibbs energy surface at z does not intersect the surface itself anywhere.

A solution to the phase equilibrium equations (1–3) yields identical fugacities for each component in all phases. This implies that the vapour phase and the liquid phase have identical tangent planes, and stability analysis by means of the tangent plane

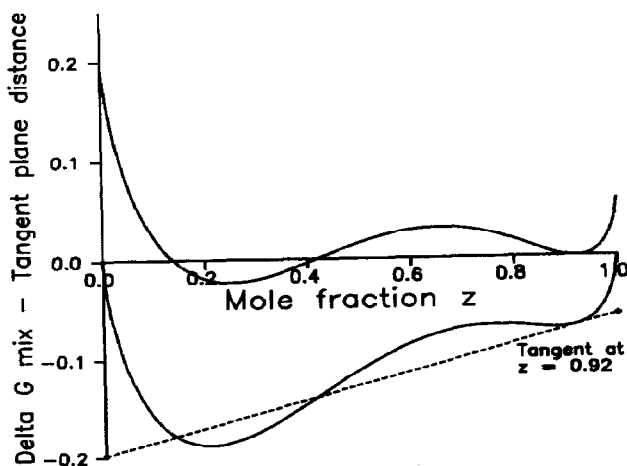


Fig. 1. Tangent plane distance plot for binary mixture.

condition thus yields identical results for both phases, or for all phases when more than two phases satisfying the equifugacity condition are present.

Verification of satisfaction of the tangent plane condition is not easy, as a search over the entire composition space is required, and in practice we shall have to assume that the condition is satisfied provided an "extensive" search does not reveal violations. Michelsen (1982a) suggested the determination of the minima of the tangent plane distance (TPD) as a means for carrying out this search. The minima of the TPD satisfy:

$$\ln f_i(\mathbf{w}) - \ln f_i(\mathbf{z}) = k, \quad (8)$$

and stability requires that k is nonnegative at all minima. Locating all solutions of equation (8) however still requires a global search, which is further complicated by the existence of a number of "trivial solutions" ($\mathbf{w} = \mathbf{z} \Rightarrow ck = 0$) corresponding to the number of equilibrium phases present. Nevertheless, guidelines for selecting trial phase compositions have been established (Michelsen, 1982a,b), and, in particular, for vapour-liquid equilibrium, converging equation (8) using "light" and "heavy" trial phases as initial estimates has proved adequate in establishing stability or instability for vapour-liquid equilibrium calculations. In multiphase systems a wider range of \mathbf{w} -compositions needs to be tested, but also here the use of the tangent plane condition appears to be the most reliable procedure yet developed (Swank and Mullins, 1986).

SPECIFICATIONS LEADING TO THERMODYNAMIC STATE FUNCTION MINIMIZATION

For a number of practically important specifications the equilibrium calculation can be formulated as a minimization of a thermodynamic state function. The best known example is the isothermal flash (specified P and T) where the solution corresponds to the global minimum of the Gibbs free energy. Other cases of practical importance, with their associated state functions, are:

(H, P) corresponding to $\min(-S)$,

(S, P) corresponding to $\min H$,

(T, V) corresponding to $\min A$,

(V, U) corresponding to $\min(-S)$.

The requirement for a global minimum implies that, except in degenerate cases, such as a pure component or an azeotropic mixture at its boiling point, the solution is unique. In addition, the tangent plane condition enables us to test whether local minima are global minima or whether they should be

characterized as false solutions. Moreover, tangent plane analysis can provide initial estimates yielding a value of the objective function lower than that of the trivial solution. The use of an iterative procedure that at each step is capable of reducing the objective function and at the same time satisfies the material balance (and specification) constraints safeguards against improper convergence to the trivial solution. Finally, tangent plane analysis enables us to attack multiphase calculations in a systematic manner.

The material balance constraints are best handled by selecting as independent variables molar amounts in one of the product phases, calculating the corresponding molar amounts in the other phase by difference from the overall feed composition, i.e. for the isothermal flash:

$$\min G(\mathbf{v}, \mathbf{l}) = \min G(\mathbf{v}, \mathbf{z} - \mathbf{v}). \quad (9)$$

The remaining cases listed above are characterized by the presence of one or two additional specification constraints, i.e. H , S , V and/or U . The nonlinearity of these constraints leads to a more complex solution procedure, e.g. nested loops based on an inner loop (P, T)-calculation, or a direct approach by means of an augmented objective function, as suggested by Michelsen (1987).

The models used for calculating thermal properties (enthalpy, entropy) occasionally differ from those used for calculating fugacities for a given phase (implying violation of the Gibbs-Helmholtz equation), the reason being that correlations for K -factors over a narrow temperature range may not be satisfactory for enthalpy. This "mild" violation of thermodynamic consistence of course makes it impossible to solve the isenthalpic and the isentropic flash by state function minimization.

The benefits from a minimization formulation should not be underrated, in particular for the very important (P, T)-case. The check for a reduction in the Gibbs energy at each iteration is a safeguard that prevents divergence at virtually no cost. It is worthwhile recognizing that such checks do not necessitate the use of special "minimization" methods but are equally applicable to classical solution procedures such as successive substitution, accelerated successive substitution or Newton's method. The only requirement for performing the check is that material balances are satisfied at each step.

The application of an algorithm that requires reduction of a corresponding objective function is not restricted to equation of state based models. In two-phase calculations with hybrid models, however, trivial solutions and near-critical behaviour are not encountered, and divergence is thus less likely to occur.

PHASE FRACTION SPECIFICATIONS

Specification of the vapour fraction β in addition to temperature or pressure is frequently encountered, in particular in the calculation of saturation points, i.e. bubble points ($\beta = 0$) or dewpoints ($\beta = 1$). When hybrid models are used, such calculations rarely present problems, and in particular bubble point calculations are very easily converged, as the incipient phase is likely to be very nearly ideal. For equation of state models, however, solutions can be very difficult to locate, as it is often not known in advance whether a single solution or multiple solutions are found, or even whether a solution to the desired specification exists.

As an example, consider the phase diagram for a typical natural gas mixture (Michelsen, 1980), shown in Fig. 2. The mixture critical point is at 58 atm, and the maximum pressure on the phase boundary is 81 atm. The number of dewpoints corresponding to a given pressure is seen to vary with the pressure as follows: below P_c we find a unique dewpoint, at pressures between P_c and P_{max} two dewpoints are found, and above P_{max} no dewpoints exist. The diagram of Fig. 2 is typical of mixtures rich in light components. For mixtures rich in heavy components, the critical point is frequently located at temperatures higher than that corresponding to P_{max} , and a similar multiplicity pattern to that shown in Fig. 2 is found for bubble points.

More complex behaviour is also possible. Hydrogen-containing mixtures often exhibit a minimum in pressure on the bubble point branch, leading to failure in the calculation of what is supposed to be the most easy saturation point calculation—the low-pressure bubble point. A more exotic example, dou-

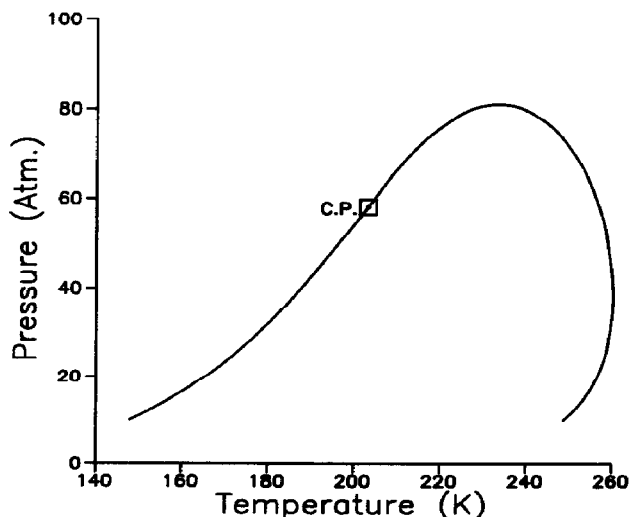


Fig. 2. Phase envelope for natural gas mixture.

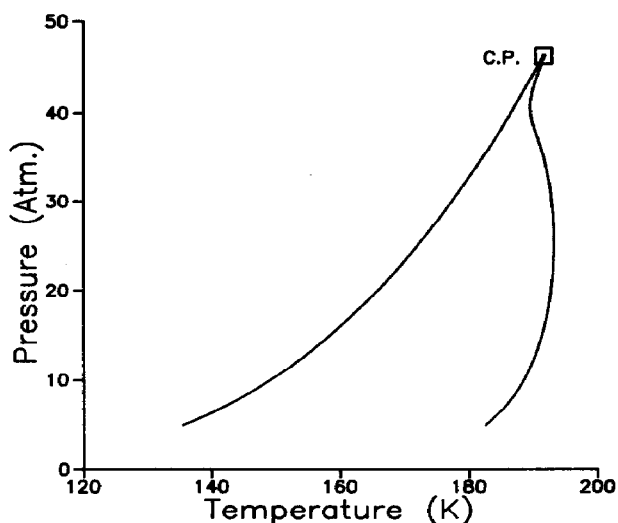


Fig. 3. Phase envelope for methane-*n*-butane binary.

bly retrograde behaviour, is observed with a very simple binary mixture, 99.9% methane and 0.1% *n*-butane, where up to 4 saturation point pressures at a given temperature are possible (Fig. 3).

A complicating factor for calculation at specified (T, β) or (P, β) is the existence of trivial solutions over an entire pressure or temperature range, as the trivial solution satisfies equations (1–3) at all conditions where the equation of state has only a single density root. Stability analysis therefore has only limited utility in validating trivial solutions in saturation point calculations.

Of course, tangent plane analysis still is useful for verifying stability or revealing instability of nontrivial solutions, e.g. false bubble points in a region where the liquid phase is unstable.

Substitution of “false roots”, i.e. densities or compressibility factors that do not satisfy the equation of state, equation (6), has been suggested as a remedy, where the properties calculated from the model appear to indicate the “wrong” phase type, e.g. a “vapour-like” phase where a liquid is desired, see e.g. Gundersen (1982). Such procedures are generally unlikely to be of much utility in the near-critical region, where the equilibrium phases only exhibit minor density differences and where it is impossible to associate a phase with being “liquid” or “vapour”, solely based on the compressibility factor. Root correction procedures are much more likely to be of help in connection with multistage calculations, where critical behaviour is less likely and where large temperature excursions in early iterations have to be managed with a modest computational effort.

In our opinion, the only safe approach for locating all potential saturation points corresponding to a given specification is by means of a “tracing” or

"continuation" method, where an entire family of solutions are calculated, starting with a point which is readily converged (hopefully), e.g. a low-pressure bubble or dewpoint calculation (Asselineau *et al.*, 1979; Michelsen, 1980). Continuation methods have found widespread use in recent years (see e.g. Wayburn and Seader, 1987) but they have actually found application for solution of chemical engineering problems for a long period, dating back at least to the "General Parameter Mapping" method of Kubicek and Hlavacek (1972). Such procedures are evidently computationally expensive, as they require determination of a number of "unwanted" solutions on the path leading to the desired solution(s), but they may present the only viable alternative when all solutions corresponding to a given specification are desired.

INDIRECT SPECIFICATIONS

A range of additional specifications of minor importance, e.g. (P, V) or (T, H) might find application, and, in general, it would be very difficult to establish in advance whether such specifications correspond to unique solutions. In the present work we shall only discuss calculations that could be characterized as "indirect specifications", i.e. specifications that relate to the character of the solution, rather than to specific properties like enthalpy or temperature. Examples are calculation of the mixture critical point, or calculation of saturation points at extremum conditions, like the maximal pressure for coexistence of two phases.

Although mixtures without critical points or mixtures with multiple critical points exist (Heidemann and Khalil, 1981), remarkably efficient procedures for location of critical points have been developed in recent years (Heidemann and Khalil, 1981; Michelsen, 1984). These procedures utilize a direct solution of the criticality conditions derived by Gibbs, preferably using volume and temperature, rather than pressure and temperature as the independent variables. It is, however, worthwhile noticing that mixture critical points can also be located by means of conventional equilibrium calculations using specifications in the form suggested earlier. As an example, specification of a vapour phase fraction of 0.5, supplemented by a specification of the K -factor of a mixture component (preferably the lightest or the heaviest) close to unity, corresponds to a near-critical state. In principle, the combination of a specified arbitrary value of the vapour fraction and a specified value close to 1 for a K -factor leads to a near-critical point, but the particular choice of $\beta = 0.5$ is associated with computational advantages, as it allows

for a greater deviation in the phase compositions (Michelsen, 1984). A critical point calculation by means of a specified vapour fraction and a specified K -factor might actually be quite easy to converge, even when composition derivatives of fugacity coefficients are unavailable, as the specification of a nonunit value for a K -factor eliminates the possibility of convergence to the trivial solution.

INDEPENDENT VARIABLES AND INITIAL ESTIMATES

The number of independent variables in eqns (1-3) can be reduced by introducing equilibrium factors defined by:

$$K_i = \frac{y_i}{x_i} \quad (10)$$

Substitution of equation (10) into the material balance equations enables determination of vapour and liquid mole fractions in terms of (β, K) , i.e.

$$x_i = \frac{z_i}{1 - \beta + \beta K_i}; \quad y_i = \frac{K_i z_i}{1 - \beta + \beta K_i} \quad (11)$$

The equilibrium equations can be written:

$$\ln K_i = \ln \phi_i^l(x, T, P) - \ln \phi_i^v(y, T, P), \quad (12)$$

and finally, the summation of mole fractions relation is written:

$$\sum_{i=1}^C z_i \frac{K_i - 1}{1 - \beta + \beta K_i} = 0. \quad (13)$$

the set of independent variables thus reduces to $C + 3$, i.e. (K, T, P, β) .

Initial estimates are frequently based on the additional assumption that the fluid phases form ideal solutions, in which vapour and liquid phase fugacity coefficients are dependent on pressure and temperature only. This implies that the K -factors are functions of only T and P , and the set of independent variables thus reduces to 3, i.e. (T, P, β) .

A commonly used approximate expression is the Wilson approximation:

$$\ln K_i = \ln\left(\frac{Pc_i}{P}\right) + 5.373(1 + \omega_i)\left(1 + \frac{Tc_i}{T}\right). \quad (14)$$

If the specification involves properties other than T , P and β , we may take this approximation one step further, assuming the vapour phase to be ideal. With this assumption, the Wilson approximation becomes:

$$\ln \phi_i^l = \ln\left(\frac{Pc_i}{P}\right) + 5.373(1 + \omega_i)\left(1 - \frac{Tc_i}{T}\right), \quad (15)$$

$$\ln \phi_i^v = 0, \quad (16)$$

which, combined with an expression for the ideal gas heat capacity enables us to calculate all derived properties.

We have in many cases found it advantageous to converge the entire calculation using physical properties calculated by means of equations (15) and (16), before involving the full model. The solution, based on this approximation, is unique for practically all specifications and provides reasonable, if not good, initial estimates for subsequent use of the full model.

The Wilson approximation is remarkably good for subcritical hydrocarbon mixtures, but the K -factors of supercritical components are overestimated, in particular for hydrogen, leading to very inaccurate initial estimates in bubble point calculations. Improved simple relations similar to the Wilson approximation are evidently desirable, but no useful alternative seems available at present.

PRACTICAL IMPLEMENTATION OF THE ISOTHERMAL FLASH

The isothermal flash, i.e. the equilibrium calculation at specified T and P , is probably the single most important phase equilibrium calculation. Fortunately it is also the specification for which an efficient and extremely robust algorithm is most readily derived. In the following, the major steps in the implementation of what we consider a robust and efficient PT-flash will be presented.

1. Initialization

Initial estimates of the K -factors are obtained from the Wilson approximation, equation (14), or, if low-pressure calculations with mixed models are performed, from pure-component vapour pressures, assuming validity of Raoult's law. The vapour fraction corresponding to the assumed K -factors is determined from equation (13), and new liquid and vapour mole fractions are subsequently calculated from equation (11).

Assuming that equation (14) yields a vapour fraction in the range $0 < \beta < 1$, the decrease in (reduced) Gibbs energy can be calculated from:

$$g_r = \frac{\Delta G}{RT} = \beta \sum_i y_i (\ln y_i + \ln \varphi_i^v) + (1 - \beta) \sum_i x_i (\ln x_i + \ln \varphi_i^l) - \sum_i z_i [\ln z_i + \ln \varphi_i(z)]. \quad (17)$$

The decrease in Gibbs energy can also be expressed in terms of reduced tangent plane distances, based on

the selection of liquid and vapour compositions as trial phases. Using [cf. equation (7)]:

$$\text{tpd}_x = \sum_i x_i [\ln x_i + \ln \varphi_i^l - \ln z_i - \ln \varphi_i(z)],$$

$$\text{tpd}_y = \sum_i y_i [\ln y_i + \ln \varphi_i^v - \ln z_i - \ln \varphi_i(z)], \quad (18)$$

the expression for the reduced Gibbs energy change be written:

$$g_r = \beta \text{tpd}_y + (1 - \beta) \text{tpd}_x. \quad (19)$$

The outcome of the initial phase split calculation is hopefully a set of compositions yielding a negative value of g_r . When this is the case we can conclude that two phases are obtained at equilibrium, and enforcing a reduction of g_r in all subsequent iteration steps eliminates the possibility of arriving at the trivial solution. Unfortunately, the initial step will frequently result in phase compositions for which tpd_x and tpd_y are both positive, or it can result in a phase fraction outside the permitted range. In the latter case we switch to stability analysis, whereas in the former, new K -factors are calculated from:

$$K_i = \varphi_i^l / \varphi_i^v \quad (20)$$

and the process can be repeated.

The continued calculation of a new phase distribution based on the fugacity coefficients from the previous step is the classical method of successive (or direct) substitution. If the subsequent steps do not rapidly result in phase compositions with negative tpd , which evidently is a prerequisite for negative g_r , our recommendation is to stop after 3 steps and continue with stability analysis, as described later. Continuation of successive substitution would be very likely to result in wasted effort, with ultimate convergence to the trivial solution for equation-of-state based calculations.

Cases are encountered where we obtain a negative value of tpd_x or tpd_y but a positive value of g_r . Assuming e.g. that tpd_x is negative, taking K -factors for the subsequent step as:

$$K_i = \varphi_i(x) / \varphi_i(z), \quad (21)$$

virtually guarantees that the subsequent step results in a negative value of g_r . Similarly, we use:

$$K_i = \varphi_i(z) / \varphi_i(y), \quad (22)$$

only when tpd_y is negative.

2. Converging the flash

Assuming that a negative g_r has been obtained, the final phase disposition is known, and our objective is to locate the equilibrium compositions as rapidly as possible. A simple and obvious candidate is

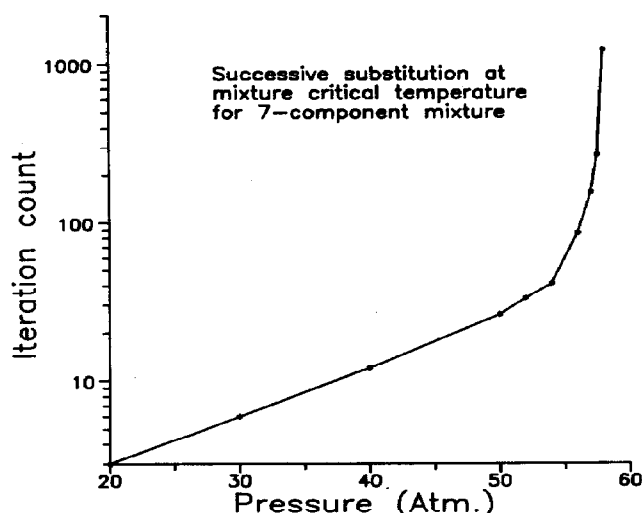


Fig. 4. Successive substitution iterations required to converge PT-flash in dependence of pressure at the mixture critical temperature.

successive substitution, which in practice turns out to be a very safe and also in many cases a fairly efficient procedure. With very few exceptions each iterative step will reduce the Gibbs energy, and convergence to the desired solution ultimately takes place. Successive substitution is implicitly based on the assumption of ideal solution behaviour, and the method is therefore particularly effective for nearly-ideal mixtures, e.g. hydrocarbons at low-to-moderate pressures. At higher pressures the rate of convergence decreases, and for near-critical mixtures convergence is exceedingly slow. The general behaviour of the method is illustrated by the convergence results of Fig. 4 where a hydrocarbon mixture at its critical temperature is flashed at pressures ranging from near-atmospheric to very close to the critical pressure.

The convergence behaviour of successive substitution has been analyzed by Michelsen (1982b), who showed that the two dominant "error reduction factors" approach a value of 1 as a critical point is reached. The fact that exactly two components of the error vector decay slowly indicates that a specific implementation of the "General Dominant Eigenvalue Method" (GDEM) of Crowe and Nishio (1975) might be particularly well-suited to accelerate convergence. Basically, the GDEM-method applies successive substitution for a number of iterations, after which an extrapolation of the correction step is attempted. The method is simple to implement and the computational overhead is insignificant. We suggest the use of three such acceleration cycles, each consisting of 5 successive substitution iterations. If convergence has not yet been obtained, we continue with a second-order minimizer.

The GDEM-acceleration typically reduces the number of iterations required by a factor of 3. It should, however, be kept in mind that the extrapolation leads to a loss of the inherent stability of the basic successive substitution process. Extrapolates should therefore only be accepted provided they lead to a reduction in the mixture Gibbs energy. Under near critical conditions GDEM frequently "over-extrapolates", with frequent failures as a result, and the use of a different approach is warranted.

Using vapour phase molar flows as the independent variables, the gradient and Hessian matrices are given by:

$$g_i = \frac{\partial}{\partial v_i} \left(\frac{G}{RT} \right) = \ln y_i + \ln \phi_i^v - \ln x_i + \ln \phi_i^l, \quad (23)$$

$$H_{ij} = \frac{\partial g_i}{\partial v_j} = \frac{1}{\beta(1-\beta)} \left(\frac{z_i}{x_i y_i} \delta_{ij} - 1 + \beta M_{ij}^l + (1-\beta) M_{ij}^v \right), \quad (24)$$

where the elements of the M -matrices are normalized partial composition derivatives of the fugacity coefficients, i.e.

$$M_{ij}^v = \left(\frac{\partial \ln \phi_i^v}{\partial v_j} \right)_{T,P}, \quad M_{ij}^l = \left(\frac{\partial \ln \phi_i^l}{\partial v_j} \right)_{T,P}. \quad (25)$$

The correction step is calculated from;

$$(\mathbf{H} + \alpha \mathbf{D}) \Delta \mathbf{v} + \mathbf{g} = 0, \quad (26)$$

where α is a stepwise correction factor chosen to ensure: (i) positive-definiteness of the modified Hessian, $\mathbf{H} + \alpha \mathbf{D}$; and (ii) a decrease in the Gibbs energy. The matrix \mathbf{D} is chosen as a diagonal matrix with elements given by $D_{ii} = z_i/x_i y_i$. Expressions for the partial composition derivatives of the fugacity coefficients (or activity coefficients) are readily derived for the majority of models of practical importance (Michelsen and Møllerup, 1986). As an alternative, the M -matrices can be approximated using a quasi-Newton approach. In this case, the procedure suggested by Venkataraman and Lucia (1986) which ensures that the approximate derivatives satisfy the Gibbs-Duhem equation, appears particularly attractive.

Most flash calculations are readily converged after the 3 cycles using the GDEM method, and second-order minimization is rarely required except in the near-critical region.

3. Stability analysis

When the initial successive substitution steps fail to reveal instability of the feed, stability analysis

by means of tangent plane distance minimization is applied. If mixed models are used, the state of the feed (liquid or vapour) is known (as that having the smaller Gibbs energy), and it is only necessary to perform the search with the alternative phase type as the trial phase. In contrast, using an equation of state frequently makes it difficult if not impossible to classify the feed as "liquid" or "vapour", and it is necessary to carry out the tangent plane distance minimization for both a "vapour-like" and a "liquid-like" trial phase. Initial composition estimates for these trial phases are calculated from:

$$w_i^v = \frac{K_i z_i}{\sum_j K_j z_j}, \quad w_i^l = \frac{z_i / K_i}{\sum_j z_j / K_j}, \quad (27)$$

using the Wilson approximation K -values.

At the minimum tpd, the following relations are satisfied [cf. equation (8)]:

$$\ln w_i + \ln \phi_i(\mathbf{w}) - \ln z_i - \ln \phi_i(\mathbf{z}) = k, \quad (28)$$

which can be reformulated in the simple "successive substitution" form:

$$\ln W_i = \ln z_i + \ln \phi_i(\mathbf{z}) - \ln \phi_i(\mathbf{w}), \quad (29)$$

$$w_i = \frac{W_i}{\sum_j W_j} \quad (30)$$

and converged by means of the GDEM method or by a second-order minimizer.

If at any stage a negative value of the tangent plane distance is encountered, the stability analysis is terminated and we proceed with the phase split calculations. Convergence of the trial phase (or both trial phases when an equation of state is used) to a nonnegative minimum or to the trivial solution $\mathbf{w} = \mathbf{z}$ is taken as an indication that the specification corresponds to a single equilibrium phase.

Although the procedure outlined above has many similarities with that suggested earlier by Michelsen (1982a,b) there are important differences. We believe that the present implementation of the two-phase flash, starting with an attempt to calculate the phase split, is more efficient than the earlier approach, since the stability analysis is avoided in situations where it is not really needed, as is the case for most practical applications. In addition the use of a second-order minimizer with strict enforcement of reduction of the objective function leads to a more robust procedure for near-critical mixtures.

SUGGESTIONS FOR FUTURE WORK

Algorithms for direct calculation of saturation points with equation-of-state based models at

elevated pressures still need development. The need for such algorithms is particularly pressing in connection with data regression, where parameters in thermodynamic models are adjusted to match experimental data. In such calculations, failure to converge "difficult" points often has the unsatisfactory consequence that data points are ignored in the regression, with resulting inferior matching ability of the model.

NOMENCLATURE

- A = Helmholtz free energy
- C = Number of components in mixture
- D = Diagonal correction matrix, equation (26)
- f_i = Fugacity of component i
- G = Gibbs energy
- g_r = Reduced Gibbs energy difference, $\Delta G/(RT)$
- \mathbf{g} = Gradient vector
- H = Enthalpy
- \mathbf{H} = Hessian matrix, second derivative of Gibbs energy
- h = Molar enthalpy
- i, j = Component indices
- K = Defined in equation (8)
- K_i = Equilibrium factor of component i , y_i/x_i
- l_i = Amount of component i in liquid
- P = Pressure
- P_{ci} = Critical pressure of component i
- S = Entropy
- T = Temperature
- T_{ci} = Critical temperature of component i
- tpd = Reduced tangent plane distance
- U = Internal energy
- V = Total volume
- v = Molar volume
- v_i = Amount of component i in vapour
- \mathbf{w} = Vector of trial phase mole fractions
- \mathbf{W} = Modified trial phase composition vector
- \mathbf{x} = Vector of liquid mole fractions
- \mathbf{y} = Vector of vapour mole fractions
- \mathbf{z} = Vector of feed mole fractions

Greek

- α = Step length control factor
- β = Vapour fraction
- ϕ_i = Component fugacity coefficient
- ω_i = Acentric factor

REFERENCES

- Asselineau L., G. Bogdanic and J. Vidal, A versatile algorithm for calculating vapour-liquid equilibria. *Fluid Phase Equilib.* 3, 273-290 (1979).
- Baker L. E., A. C. Pierce and K. D. Luks, Gibbs energy analysis of phase equilibrium. *Soc. Petrol. Engrs JI Oct*, 731-742 (1982).
- Crowe A. M. and M. Nishio, Convergence promotion in the simulation of chemical processes—the general dominant eigenvalue method. *AIChE JI* 21, 528-533 (1975).
- Gundersen T., Numerical aspects of the implementation of cubic equations of state in flash calculation routines. *Computers chem. Engng* 6, 245-255 (1982).
- Heidemann R. A. and A. M. Khalil, The calculation of critical points. *AIChE JI* 26, 769-779 (1980).
- Kubicek M. and V. Hlavacek, Solution of nonlinear

- boundary value problems—Va: a novel method: general parameter mapping (GPM). *Chem. Engng Sci.* **27**, 743–760 (1972).
- Michelsen M. L., Calculation of phase envelopes and critical points for multicomponent mixtures. *Fluid Phase Equilib.* **4**, 1–10 (1980).
- Michelsen M. L., The isothermal flash problem. Part I: stability. *Fluid Phase Equilib.* **9**, 1–19 (1982a).
- Michelsen M. L., The isothermal flash problem. Part II: phase split calculation. *Fluid Phase Equilib.* **9**, 20–39 (1982b).
- Michelsen M. L., Calculation of critical points and of the phase boundary in the critical region. *Fluid Phase Equilib.* **16**, 57–76 (1984).
- Michelsen M. L., Multiphase isenthalpic and isentropic flash algorithms. *Fluid Phase Equilib.* **33**, 13–27 (1987).
- Michelsen M. L. and J. Mollerup, Partial derivatives of thermodynamic properties. *AIChE JI* **32**, 1389–1392 (1986).
- Swank D. J. and J. C. Mullins, Evaluation of methods for calculating liquid–liquid phase splitting. *Fluid Phase Equilib.* **30**, 101–110 (1986).
- Venkataraman S. and A. Lucia, Exploiting the Gibbs–Duhem equation in separation calculations, *AIChE JI* **32**, 1057–1066 (1986).
- Wayburn T. L. and J. D. Seader, Homotopy continuation methods for computer aided process design. *Computers chem. Engng* **11**, 7–26 (1987).