THE ISOTHERMAL FLASH PROBLEM. PART II.
PHASE-SPLIT CALCULATION

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ABSTRACT


Algorithms for calculation of multiphase equilibrium at given temperature and pressure using a single Equation of State as the thermodynamic model are described. The use of stability analysis to generate initial estimates and of second order convergence methods lead to rapid solution even in the immediate vicinity of critical points.

INTRODUCTION

Single-stage phase equilibrium calculations typically involve specification of a feed composition and two additional separation variables, normally selected from temperature \(T\), pressure \(P\), vapour fraction \(V\), enthalpy \(H\), entropy \(S\), a phase yield or a phase mole fraction. When a single Equation of State is used as the thermodynamic model for both fluid phases such a set of specifications may not uniquely define the solution since a given set may correspond to several valid solutions. As an example we can consider dew-point calculations for a mixture where the maximal pressure on the phase boundary is higher than the critical pressure. Specification of a pressure between the critical and the maximal leads to two solutions and specifications of a pressure higher than the maximal gives no solution to the problem. Specifications which may correspond to multiple solutions are best solved indirectly by a tracing technique (Michelsen, 1980) when all solutions are desired.

Certain practically important specifications do however guarantee a unique solution. This is the case for specified \(T\) and \(P\), where the solution corresponds to the global minimum in the Gibbs energy, and also for specified
(P,H) and (P,S) corresponding to maximal entropy and minimal enthalpy, respectively. This type of specification is best handled by a direct approach, and procedures for the P–T flash calculation are discussed in this paper.

A severe problem is that even though the solution is known to be unique, the number of equilibrium phases and hence the number of independent variables is not known in advance. For this reason we suggest that flash problems which may involve more than two fluid phases are treated in a stepwise manner, using alternatively the stability analysis described in a preceding paper (Michelsen, 1981a) to decide whether a given solution is stable, that is, whether a minimum in Gibbs energy is global, and a local minimization procedure described in the following to obtain a constrained minimum corresponding to a given number of phases.

VAPOUR–LIQUID EQUILIBRIUM

The majority of flash processes of industrial interest involve only a vapour phase and a single liquid phase. When it is known in advance that a given mixture at the specified temperature and pressure is incapable of forming multiple liquid phases it is fairly easy to decide whether a vapour–liquid phase split will occur (Michelsen, 1981a). Methods for calculating the phase split for specifications in the two-phase region and problems associated with the calculation are discussed in the following.

The direct substitution method

Direct substitution is the traditional method of solution for two-phase vapour–liquid equilibrium calculations at given T and P (Henley and Rosen, 1969; King, 1980). Let the mole fractions of component i in the liquid and vapour phases be x_i and y_i, respectively, and define the equilibrium factor K_i = y_i/x_i.

Material balance constraints yield

\[ x_i = \frac{z_i}{1 + (K_i - 1) V} \]  
\[ y_i = \frac{K_i z_i}{1 + (K_i - 1) V} \]

where V is the vapour phase fraction.

The value of V corresponding to an assumed set of K-factors is found solving the flash equation:

\[ F(V) = \sum_i (y_i - x_i) = \sum_i z_i (K_i - 1) / (1 + (K_i - 1) V) = 0 \]

\( F(V) \) is monotonically decreasing and a root \( 0 < V < 1 \) exists provided

\[ \sum_i K_i z_i > 1, \quad \sum_i z_i / K_i > 1 \]
At equilibrium $x_i \phi_i(x) = y_i \phi_i(y)$, where $\phi_i$ is the fugacity coefficient of component $i$. Hence we must have

$$K_{i, eq} = \frac{\phi_i(x)}{\phi_i(y)}$$

(5)

Mole fractions ($x,y$) corresponding to the value of $V$ found from (3) are calculated from eqns. (1) and (2), and the $K_{i, eq}$ are evaluated from the thermodynamic model. If the resulting $K_i$ do not agree with the assumed to within the desired tolerance, the process is repeated, starting with $K_i$ from (5).

Direct substitution converges rapidly for problems where the fugacity coefficients are only weakly dependent on the phase composition, e.g. for hydrocarbon mixtures at low pressures.

Since the individual $K_i$ may vary by orders of magnitude it is customary to use their logarithms as the actual iteration variables. The direct substitution procedure is linearly convergent with a rate determined by the numerically largest eigenvalue of the matrix $S$ given by

$$S_{ij} = \left( \frac{\partial \ln K_i^{(t+1)}}{\partial \ln K_j^{(t)}} \right)_{t \to \infty}$$

where $t$ is the iteration number. Convergence requires that $|\lambda|_{\text{max}} < 1$, and in appendix A is shown that the converged solution will always represent a local (if not global) minimum in the system Gibbs energy.

A phase envelope for a typical natural gas mixture is shown in Fig. 1. The three largest eigenvalues of $S$ for the flash compositions at a number of points in the $(T,P)$-plane are given in Table 1. The SRK-equation (Soave,

Fig. 1. Phase envelope for a seven-component mixture calculated from the SRK-equation.
TABLE 1
The three numerically largest eigenvalues of S for a series of points in the \((P-T)\)-plane for mixture of Fig. 1

<table>
<thead>
<tr>
<th>Point</th>
<th>Temperature (K)</th>
<th>Pressure (atm)</th>
<th>Eigenvalues of S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(\lambda_1)</td>
</tr>
<tr>
<td>A</td>
<td>165.50</td>
<td>20.0</td>
<td>0.133</td>
</tr>
<tr>
<td>B</td>
<td>187.60</td>
<td>40.0</td>
<td>0.307</td>
</tr>
<tr>
<td>C</td>
<td>196.40</td>
<td>50.0</td>
<td>0.739</td>
</tr>
<tr>
<td>D</td>
<td>202.56</td>
<td>57.41</td>
<td>0.997</td>
</tr>
<tr>
<td>E</td>
<td>203.13</td>
<td>58.10</td>
<td>0.999</td>
</tr>
<tr>
<td>F</td>
<td>203.0</td>
<td>57.0</td>
<td>0.934</td>
</tr>
<tr>
<td>G</td>
<td>204.0</td>
<td>58.0</td>
<td>0.938</td>
</tr>
<tr>
<td>H</td>
<td>204.12</td>
<td>59.32</td>
<td>0.996</td>
</tr>
<tr>
<td>I</td>
<td>213.0</td>
<td>70.0</td>
<td>0.872</td>
</tr>
<tr>
<td>J</td>
<td>227.10</td>
<td>80.0</td>
<td>0.675</td>
</tr>
<tr>
<td>K</td>
<td>258.47</td>
<td>25.0</td>
<td>0.076</td>
</tr>
<tr>
<td>Critical</td>
<td>203.125</td>
<td>58.108</td>
<td>1.0</td>
</tr>
</tbody>
</table>

1972) using parameters listed in Reid et al. (1977) is used as the thermodynamic model for both fluid phases in this work. We observe that at low pressures all eigenvalues are small, but that two eigenvalues approach unity in the vicinity of the critical point. We can show, in analogy with Michelsen (1981a), that for two-parameter cubic Equations of State, where all the binary interaction coefficients equal zero, only three eigenvalues of S are nonzero, regardless of the number of components.

The number of iterations required to obtain convergence is inversely proportional to the logarithm of the largest eigenvalue, and clearly acceleration is needed in the critical region. The low effective rank of S makes the direct substitution method well suited for acceleration. Among the methods suggested are gradient extrapolation (Mehra et al., 1980a) and Broyden updating using the identity matrix as the initial estimate of the inverse Jacobian (Boston and Britt, 1978).

We have found the General Dominant Eigenvalue Method of Crowe and Nishio (1975) particularly useful, assuming, in line with the behaviour in the critical region, that only two eigenvalues are of appreciable magnitude. This method is in our experience as efficient as that of Boston and Britt (1978) for the flash problem, and the computational overhead is very small.

Two major problems arise in connection with any algorithm for the isothermal flash. The first is the selection of initial estimates and the second is to ensure rapid convergence near the critical point.
Initial estimate selection

The proper selection of initial estimates is particularly important near the phase boundary in the critical region. At low pressures initial estimates based on Raoult's law are satisfactory, but at high pressures the result is frequently that after a few iterations a root of eqn. (5) in the interval (0, 1) can no longer be found.

Let us for example assume that our $K$-factor estimate is such that $\sum z_i / K_i < 1$, corresponding to a value of $V$ greater than one. One might proceed as follows:

Take $V = 1$ and obtain from eqns. 1, 2:

\[
x_i = z_i / K_i, \quad y_i = z_i
\]

where $\sum x_i < 1$. The $x_i$ are normalized, and new $K$-factors are evaluated from

\[
K_i = \phi_i(x) / \phi_i(y) = \phi_i(x) / \phi_i(z)
\]

Continuing in this manner yields, as long as no root of $V$ in the desired interval can be found, the following iteration sequence for the $x_i$

\[
\ln x_i^{(t+1)} = \ln z_i + \ln \phi_i(z) - \ln \phi_i(x^{(t)})
\]

This corresponds exactly to direct substitution for the stability analysis recommended by Michelsen (1981a). Equation (9) can lead to a set of $x$-values where $\sum x_i > 1$ showing that the mixture is unstable. In this case eqn. (4b) is again satisfied, and the flash calculation can be resumed. A second possibility is convergence to the trivial solution $x = z$. Unfortunately this does not permit us to conclude that the specification is in the one-phase region. We have frequently observed that a specification close to the phase boundary on the bubble point side leads to violation of eqn. (4b) at an early stage. Continuing with eqn. (9) corresponds to a search for a liquid phase, where the correct solution is a vapour phase present in a small amount.

To obtain a safe initial estimate and to avoid unnecessary computation a much better approach is to use the two-sided stability analysis described in Michelsen (1981a) in all cases where it is not immediately obvious that the $(P,T)$-specification is in the two-phase region. If the stability analysis verifies that the specification is in the two-phase region we automatically obtain a phase composition estimate, and this estimate is particularly accurate close to the phase boundary where convergence is normally most difficult to obtain.

Positive definiteness of the Hessian matrix

The second problem is connection with isothermal flash algorithms is of an entirely different nature and will not affect the basic direct substitution
method but only the various acceleration methods, including a complete Newton–Raphson solution. It arises whenever the matrix of second derivatives $B$ of the system Gibbs energy with respect to the independent iteration variables is not positive definite. This may happen for a specification in the intrinsically unstable region (see Fig. 3 of Michelsen, 1981a). The problem is illustrated schematically in Fig. 2, where a minimum of a one-dimensional function must be located.

The difference between assumed and calculated $K$-factors is a measure of the gradient of the Gibbs energy (Mehra et al., 1980a), and the accelerated direct substitution methods attempt to locate a point where the gradient equals zero.

We note in Fig. 2 that a search for a zero of $f'$, starting from point $a$, will lead in the wrong direction.

If $B$ is not positive definite subsequent iterates for direct substitution will appear to diverge initially, but ultimately converge to the desired solution. Damping should not be used since it will only increase the number of iterations required. If acceleration is used in such situations it is necessary to check that new iterates actually lead to a decrease in Gibbs energy.

The problem is most efficiently handled by a judicious selection of the initial estimates. Starting from point $b$ in Fig. 2 for example will lead to smooth convergence.

The stability analysis suggested by Michelsen (1981a) does provide initial estimates which makes it unlikely that $B$ becomes indefinite during iterations. A specification in the region of intrinsic instability leads to a nontrivial solution of the stability investigation for both the liquid-like and the vapour-like trial phase. The $K$-factors are then selected as the ratio of the

Fig. 2. Minimization of a one-dimensional function.
fugacity coefficients for the liquid type solution to those of the vapour type solution, and acceleration is unproblematic.

**Convergence method**

Our recommended approach is to use stability analysis for obtaining initial $K$-factor estimates, followed by direct substitution with GDEM-acceleration. Only two acceleration steps are taken, each after 5 steps of direct substitution. If convergence is not obtained final calculations are done using a full Newton–Raphson method. This procedure has succeeded for all systems investigated involving only vapour–liquid equilibrium, even in the immediate vicinity of the critical point.

The number of final Newton–Raphson iterations required to converge a series of $(P,T)$-specifications for the mixture shown in Fig. 1 is given in Table 2. As convergence criterion is used that $\Sigma (\Delta \ln K)^2 < 10^{-14}$, yielding essentially machine accuracy (15 digits). The implementation is described in Appendix B.

Broyden updating or GDEM could be used as well for the final convergence, but both are uneconomical close to the critical point. The Broyden method of Boston and Britt (1978) requires for point D a change in the determinant of the Jacobian of five orders of magnitude (see Appendix B), and calculations are likely to diverge unless stepsize restrictions are imposed. The cost involved in using the Newton–Raphson method with analytic derivatives is modest. Partial composition derivatives of the fugacity coefficients are needed, and these can, as described in Michelsen (1981b), for cubic Equations of State be evaluated at a cost of approximately twice that required for fugacity coefficients only. Finally the Newton–Raphson method provides at very little additional cost a set of complete and exact sensitivities, i.e. the derivatives of the solution vector with respect to the specification variables $T$ and $P$. Such sensitivities are useful for sequential calculations at new specifications close to the original. A new application of the sensitivities, calculation of critical points on multiphase boundaries, is described in Appendix C.

**TABLE 2**

<table>
<thead>
<tr>
<th>Point</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of iterations</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>4</td>
<td>3</td>
<td>4</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Number of Newton–Raphson iterations required to converge $(R–T)$ specifications of Table 1
MULTIPHASE EQUILIBRIUM

When an equilibrium stage with more than a single liquid phase is possible the simple approach used for the vapour-liquid flash is insufficient. A stepwise procedure is suggested, where stability analysis and phase split calculations are performed alternatively. The stability analysis indicates whether the system Gibbs energy can be decreased by forming an additional phase, and the phase split calculation determines the phase compositions corresponding to minimal Gibbs energy for a given number of phases. The procedure used for stability analysis of multiphase systems is described earlier (Michelsen, 1981a), and schemes applicable for the phase split calculations are presented below.

Direct substitution for multiphase systems

Direct substitution can be used as well for multiphase systems, the J-phase analogue of eqn. (3) being

\[ \sum_{i} z_{i}(K_{im} - 1)/H_{i} = 0, \quad m = 1, 2, \ldots, J - 1 \]  \hspace{1cm} (10)

where

\[ H_{i} = 1 + \sum_{m=1}^{J-1} V_{m}(K_{im} - 1) \]  \hspace{1cm} (11)

\( V_{m} \) being the fraction of phase \( m \).

In eqn. (10) \( K_{im} \) is defined at the ratio of the mole fraction of component \( i \) in phase \( m \) to its mole fraction in phase \( J \).

Solution of eqns. 10 and 11 for the \( J - 1 \) phase fractions \( V_{m} \) by Newton–Raphson iteration is unproblematic.

Phase compositions are subsequently found from

\[ y_{im} = z_{i}K_{im}/H_{i}, \quad m = 1, 2, \ldots, J - 1 \]  \hspace{1cm} (12)

\[ y_{iJ} = z_{i}/H_{i} \]  \hspace{1cm} (13)

and new \( K \)-factors can be evaluated from the thermodynamical model.

Initial estimates for the \( K \)-factors or the phase compositions are available from stability analysis for the preceding \( J - 1 \) phase solution.

Multiphase systems involve at most one vapour phase, the remaining being liquid, and except for highly immiscible liquid phases the direct substitution method is normally very slow. Strongly non-ideal behaviour is often taken as the prime indication for acceleration being advantageous or necessary. This is not the case. Hydrocarbon-water mixtures involving a liquid hydrocarbon phase and liquid water converge in few iterations without
acceleration. The difficult systems are those which exhibit a fairly narrow immiscibility region.

GDEM is again recommended for acceleration of direct substitution, and we suggest to use three acceleration steps. It is evident that the number of non-zero eigenvalues of $S$ increases with an increasing number of phases, but we found no significant advantage in using more than two terms in acceleration.

Second order methods

Problems which can not be converged in this manner occur relatively frequently in multiphase systems. Since we can no longer expect that our selection of initial estimates yields a positive definite matrix of second derivatives of the Gibbs energy, Newton–Raphson iteration is not well suited for final convergence of difficult problems. Instead is used Gibbs energy minimization by the method of Murray (1972). The Murray method is essentially a Newton–Raphson iteration for zero gradient. A modified Cholesky decomposition of the Hessian matrix is employed, and in case the Hessian matrix is positive definite the Murray method does not differ from the Newton–Raphson method. If $B$ is not positive definite modifications are made during the decomposition in such a manner that a positive definite matrix, which deviates as little as possible from the true Hessian, is used. The modifications guarantee that a descent direction is found. Iteration steps are only accepted provided they lead to a decrease in the Gibbs energy, and a line search is occasionally required, in particular when $B$ is not positive definite. The use of a method where each new iterate is characterized by a lower Gibbs energy is important, since this ensures that we can never return to the trivial solution.

A second order method was also used by Mehra et al. (1980b) for computation of multiphase equilibria. They employed a Levenberg–Marquardt procedure for minimization of the gradient norm. The procedure is efficient and reliable but computationally more expensive than the Murray method. Also, as recognized by the authors, it is incapable of handling an indefinite Hessian matrix, and it was necessary to switch to a gradient extrapolation method when a sign change in the determinant of the Jacobian was observed.

The Newton method suggested by Gautam and Seider (1979) for Gibbs energy minimization in computation of combined physical and chemical equilibrium has no problems with indefiniteness since the partial composition derivatives of the fugacity coefficients are ignored in the construction of the Hessian. As a result, however, convergence will be rather slow except for nearly ideal mixtures.
Independent variables

As independent variables in the Gibbs energy minimization are used the yield fractions $\theta_{im}$ defined as

$$\theta_{im} = \frac{V_m y_{im}}{z_i} \quad (14)$$

The yield fractions satisfy $\sum_m \theta_{im} = 1$, and for each species one of the $\theta_{im}$ becomes a dependent variable. We select, in analogy with Mehra et al. (1980b), as the dependent variable for component $i$

$$\theta_i = \max_m (\theta_{im}) \quad (15)$$

The elements of the gradient vector are

$$\frac{\partial}{\partial \theta_{im}} \left( \frac{G}{RT} \right) = z_i \{ (\ln y_{im} + \ln \phi_{im}) - (\ln y_{iM} + \ln \phi_{iM}) \} \quad (16)$$

and the Hessian matrix is found from

$$\frac{\partial^2}{\partial \theta_{jk} \partial \theta_{im}} \left( \frac{G}{RT} \right) = z_i z_j \left\{ \frac{(\delta_{ik} - \delta_{ik})}{V_m} \left( \frac{\delta_{ij}}{y_{im}} - 1 + \frac{\partial}{\partial n_j} \phi_{im} \right) - \frac{(\delta_{ik} - \delta_{ik})}{V_m} \right\} \times \left( \frac{\delta_{ij}}{y_{iM}} - 1 + \frac{\partial}{\partial n_j} \phi_{iM} \right) \quad (17)$$

where

$$\theta_{ij} = \max_k (\theta_{jk}) \quad (18)$$

A gradient norm less than $10^{-8}$ is used as the convergence criterion. Iterations are performed without re-evaluation of the Hessian matrix provided the gradient norm is reduced by at least a factor of 10.

Removal of phases

It is occasionally necessary to remove a phase during phase-split calculations with more than two phases present. This is done by testing before each evaluation of the Hessian whether the total Gibbs energy of the system can be decreased by combining the phase present in the smallest amount with one of the other phases. If this is the case the phases are combined and calculations are continued with a reduced number of phases.

The removal of a phase is normally observed for a specification in the liquid–liquid region very close to the three-phase boundary. The initial stability investigation shows that the Gibbs energy can be reduced by forming a vapour phase. The vapour–liquid solution is unstable and a new liquid phase is formed, resulting ultimately in the vanishing of the vapour phase.
The situation will not arise if the initial stability investigation leads to formation of a second liquid phase. The instability with respect to a vapour phase is however more readily detected, and we stop the stability analysis as soon as instability is verified to avoid unnecessary computation.

**Simplifications**

For systems containing components present in trace amounts or components that for practical purposes do not distribute into all phases, simplifications are possible. Trace components can be removed completely from the list of independent variables, and their distribution can after each iteration be calculated from the values of their infinite dilution fugacity coefficients in the phases present. This reduction saves \( J - 1 \) variables for each trace component. Non-distributing or partly distributing components can be handled similarly. In three-phase hydrocarbon–water systems the hydrocarbon content in the liquid water phase is negligible, and it can again be calculated from infinite dilution fugacity coefficients. Hence only one yield fraction for each hydrocarbon is needed.

The modifications do not effect the correctness of the final solution since the Gibbs energy and the gradient vector is calculated for the full range of components. The procedure still essentially exhibits quadratical convergence provided the concentration level below which components are considered to be present in trace amounts is selected appropriately. Here this selection is based on the outcome of the stability analysis. A large (negative) tangent plane distance indicates an easy problem where a fairly high threshold level can be permitted, whereas marginal instability calls for a more cautious approach.

**Test examples**

We shall finally present some test examples from a nitrogen-rich light-hydrocarbon mixture, which exhibits unexpectedly complicated behaviour. The mixture composition and the phase diagram are shown in Fig. 3. The mixture has, according to SRK-thermodynamics, two separate three-phase regions and a total of six critical points, with three located on the two-phase boundary, two on the boundary of the upper three-phase region and one on the lower three-phase boundary. The critical points on the three-phase boundaries were calculated by a new procedure described in Appendix C. The three-phase boundary was constructed by a method similar to that used by Michelsen (1980) for the two-phase boundary.

The critical points are listed in Table 3, and selected points on boundaries of the very narrow three-phase regions are given in Table 4.
The first example, shown in Table 5, corresponds to a specification in the liquid–liquid region close to the three-phase boundary. A vapour–liquid solution is found initially, and during the first Murray-iteration in the attempted three-phase solution the vapour phase is removed. Convergence is obtained after one additional iteration. The iteration count refers to the number of evaluations of the Hessian matrix.

The second example shown in Table 6 is for a three-phase solution. Here we note that even though the second liquid phase is present in an appreciable amount, the change in Gibbs energy going from two to three phases is three orders of magnitude smaller than the energy change from one to two phases.

### TABLE 3
Critical points for 6-component mixture shown in Fig. 3

<table>
<thead>
<tr>
<th>T_c (K)</th>
<th>P_c (atm)</th>
<th>Boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td>86.13</td>
<td>927.62</td>
<td>Two-phase</td>
</tr>
<tr>
<td>140.70</td>
<td>35.63</td>
<td>Two-phase</td>
</tr>
<tr>
<td>168.44</td>
<td>89.07</td>
<td>Two-phase</td>
</tr>
<tr>
<td>106.07</td>
<td>6.39</td>
<td>Three-phase</td>
</tr>
<tr>
<td>135.52</td>
<td>24.73</td>
<td>Three-phase</td>
</tr>
<tr>
<td>169.37</td>
<td>60.79</td>
<td>Three-phase</td>
</tr>
</tbody>
</table>
TABLE 4
Lower and upper temperature of three phase boundaries at selected pressures

<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>$T_1$(K)</th>
<th>$T_2$(K)</th>
<th>Region</th>
</tr>
</thead>
<tbody>
<tr>
<td>60.0</td>
<td>168.47</td>
<td>169.19</td>
<td>Upper</td>
</tr>
<tr>
<td>50.0</td>
<td>159.76</td>
<td>161.15</td>
<td></td>
</tr>
<tr>
<td>40.0</td>
<td>150.97</td>
<td>151.79</td>
<td></td>
</tr>
<tr>
<td>30.0</td>
<td>141.24</td>
<td>141.49</td>
<td></td>
</tr>
<tr>
<td>21.10</td>
<td>131.07</td>
<td>131.07</td>
<td></td>
</tr>
<tr>
<td>15.88</td>
<td>123.93</td>
<td>123.93</td>
<td>Lower</td>
</tr>
<tr>
<td>14.0</td>
<td>121.02</td>
<td>121.05</td>
<td></td>
</tr>
<tr>
<td>12.0</td>
<td>117.66</td>
<td>117.74</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>173.92</td>
<td>114.07</td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>109.68</td>
<td>109.92</td>
<td></td>
</tr>
</tbody>
</table>

Finally Table 7 shows a calculation in the three-phase region close to the vapour–liquid critical point. The two-phase solution found initially is best characterized as liquid–liquid equilibrium, and the formation of the third-phase (a vapour) has almost no effect on the Gibbs energy.

The total computing time for these three examples is 0.6 s on an IBM 3033 (FORTH compiler). A complete output is obtainable on request from the author.

TABLE 5
Phase split calculations for mixture of Fig. 3 at $T = 150.9$ K; $P = 40$ atm

<table>
<thead>
<tr>
<th>Phase fraction</th>
<th>Initial split</th>
<th>Final solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.031</td>
<td>0.969</td>
</tr>
<tr>
<td>Phase compressibility</td>
<td>0.573</td>
<td>0.158</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component mole fractions</th>
<th>Initial split</th>
<th>Final solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>0.716</td>
<td>0.291</td>
</tr>
<tr>
<td>$C_1$</td>
<td>0.282</td>
<td>0.556</td>
</tr>
<tr>
<td>$C_2$</td>
<td>0.002</td>
<td>0.073</td>
</tr>
<tr>
<td>$C_3$</td>
<td>$1.3 \times 10^{-4}$</td>
<td>0.038</td>
</tr>
<tr>
<td>$nC_4$</td>
<td>$1.0 \times 10^{-5}$</td>
<td>0.021</td>
</tr>
<tr>
<td>$nC_5$</td>
<td>$1.1 \times 10^{-6}$</td>
<td>0.020</td>
</tr>
</tbody>
</table>

Gibbs energy changes, $(\Delta G/RT)$: $L \rightarrow LV$: $-1.78 \cdot 10^{-4}$; $LV \rightarrow LL$: $-1.39 \cdot 10^{-4}$

Murray iterations: $L \rightarrow LV$: 0; $LV \rightarrow LL$: 2
TABLE 6
Phase split calculations for mixture of Fig. 3 at $T = 151.7$ K; $P = 40$ atm

<table>
<thead>
<tr>
<th>Phase fraction</th>
<th>Initial split</th>
<th>Final solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>0.056</td>
<td>0.053</td>
</tr>
<tr>
<td>$C_1$</td>
<td>0.579</td>
<td>0.579</td>
</tr>
<tr>
<td>$C_2$</td>
<td>0.291</td>
<td>0.291</td>
</tr>
<tr>
<td>$C_3$</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>$n-C_4$</td>
<td>0.579</td>
<td>0.579</td>
</tr>
<tr>
<td>$n-C_5$</td>
<td>0.157</td>
<td>0.157</td>
</tr>
</tbody>
</table>

Component mole fractions

<table>
<thead>
<tr>
<th>Component mole fractions</th>
<th>Initial split</th>
<th>Final solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>0.707</td>
<td>0.707</td>
</tr>
<tr>
<td>$C_1$</td>
<td>0.280</td>
<td>0.291</td>
</tr>
<tr>
<td>$C_2$</td>
<td>0.075</td>
<td>0.002</td>
</tr>
<tr>
<td>$C_3$</td>
<td>0.157</td>
<td>0.139</td>
</tr>
<tr>
<td>$n-C_4$</td>
<td>0.053</td>
<td>0.159</td>
</tr>
<tr>
<td>$n-C_5$</td>
<td>0.157</td>
<td>0.157</td>
</tr>
</tbody>
</table>

Gibbs energy changes, $\left( \Delta G / RT \right)$: $L \rightarrow LV:\ -6.04 \cdot 10^{-4}$; $LV \rightarrow LLV:$ $-1.25 \cdot 10^{-6}$

Murray iterations: $L \rightarrow LV: 0$; $LV \rightarrow LLV: 2$

TABLE 7
Phase split calculations for mixture of Fig. 3 at $T = 169$ K; $P = 60.5$ atm

<table>
<thead>
<tr>
<th>Phase fraction</th>
<th>Initial split</th>
<th>Final solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>0.340</td>
<td>0.006</td>
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<tr>
<td>$C_1$</td>
<td>0.660</td>
<td>0.334</td>
</tr>
<tr>
<td>$C_2$</td>
<td>0.319</td>
<td>0.350</td>
</tr>
<tr>
<td>$C_3$</td>
<td>0.230</td>
<td>0.230</td>
</tr>
</tbody>
</table>

Phase mole fractions

<table>
<thead>
<tr>
<th>Phase mole fractions</th>
<th>Initial split</th>
<th>Final solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>0.454</td>
<td>0.481</td>
</tr>
<tr>
<td>$C_1$</td>
<td>0.226</td>
<td>0.454</td>
</tr>
<tr>
<td>$C_2$</td>
<td>0.566</td>
<td>0.493</td>
</tr>
<tr>
<td>$C_3$</td>
<td>0.094</td>
<td>0.512</td>
</tr>
<tr>
<td>$n-C_4$</td>
<td>0.053</td>
<td>0.025</td>
</tr>
<tr>
<td>$n-C_5$</td>
<td>0.031</td>
<td>0.053</td>
</tr>
</tbody>
</table>

Gibbs energy changes, $\left( \Delta G / RT \right)$: $L \rightarrow LL:\ -3.35 \cdot 10^{-3}$; $LL \rightarrow LLV:$ $-6.2 \cdot 10^{-10}$

Murray iterations: $L \rightarrow LL: 0$; $LL \rightarrow LLV: 2$

Conclusion and suggestion for further work

Computational algorithms have been developed for the calculation of multiphase equilibrium at specified temperature and pressure. The algorithms require no user-provided initial estimates and are capable of automatic determination of the number of phases present at equilibrium. Newton–Raphson iteration for vapour–liquid equilibrium problems and Gibbs
energy minimization using the second order minimization algorithm of Murray (1972) leads to safe convergence at low computational cost in critical regions.

The present algorithms are developed for use with a single Equation of State for calculation of all thermodynamic properties, but different models for the fluid phase can be used as well (Michelsen and Magnussen, 1982).

Adaption of the multiphase algorithm to include solid phases is straightforward, and modifications for alternative specifications corresponding to a unique equilibrium state, e.g. pressure and enthalpy or pressure and entropy, are currently being investigated.

ACKNOWLEDGEMENT

The author thanks Linde A/G, Munich, West Germany, for their interest in this work and their cooperation in extensive testing of the algorithms. In particular, the many suggestions for improvement from Dr. Hubert Franke and Dr. Hans Kistenmacher, Linde A/G, are appreciated.

APPENDIX A: CONVERGENCE OF THE DIRECT SUBSTITUTION METHOD

We consider at given $T$ and $P$ 1 mol of a mixture of composition $(z_1, z_2, \ldots, z_N)$ splitting into two phases with mole numbers $(l_1, l_2, \ldots, l_N)$ and $(l_1', l_2', \ldots, l_N')$ where $l_i + l_i' = z_i$. As independent variables are selected the $l_i$.

The phase split represents a stationary point in Gibbs energy provided

$$\frac{\partial G}{\partial l_i} = 0, \quad i = 1, 2, \ldots, N \quad (A1)$$

or

$$RT\left[\ln l_i - \ln L + \ln \phi_i^L - \ln \phi_i^V\right] = 0 \quad (A2)$$

where $L = \sum_i l_i$, $V = \sum_i v_i - 1 - L$.

The stationary point is a local minimum if the Hessian matrix is positive definite.

We obtain

$$B_{ij} = \frac{\partial^2 \left( \frac{G}{RT} \right)}{\partial l_i \partial l_j} = \left( \frac{\delta_{ij}}{l_i} - \frac{1}{L} + \frac{\partial \ln \phi_i^L}{\partial n_j} \right) + \left( \frac{\delta_{ij}}{v_i} - \frac{1}{V} + \frac{\partial \ln \phi_i^V}{\partial n_j} \right) \quad (A3)$$

or $B = Q + \Phi \quad (A4)$

where:

$$Q_{ij} = \frac{\delta_{ij}}{l_i} + \frac{\delta_{ij}}{v_i} - \left( \frac{1}{L} + \frac{1}{V} \right) \quad (A5)$$
It is easily shown that except in the trivial case \( \frac{l_i}{L} = \frac{v_i}{V} \), all \( Q \) is positive definite.

Hence we may write

\[
Q = EE^T
\]  

and

\[
B = E(I + E^{-1} \Phi E^{-T}) E^T = ECET
\]  

and \( B \) is positive definite provided \( C \) is positive definite.

Direct substitution will converge to a solution where all eigenvalues of the matrix \( S \) (eqn. 6) at the solution are numerically smaller than one.

\[
S_{ij} = \frac{\partial \ln K_j}{\partial \ln K_j} - \frac{\partial}{\partial \ln K_j} \{ \ln \phi_i^L - \ln \phi_i^R \}
\]

or \( S = \Phi D \) with \( D_{ij} = \frac{\partial l_i}{\partial \ln K_j} \)

From \( \frac{\partial \ln K_i}{\partial l_j} = \frac{\partial}{\partial l_j} \{ \ln(v_i/V) - \ln(l_i/L) \} = -Q_{ij} \)

we see that \( D = -Q^{-1} = -E^{-T}E^{-1} \)

An eigenvalue-eigenvector pair of \( S \) satisfies

\[
Su = \lambda_s u
\]

or \(-\Phi E^{-T}E^{-1} u = \lambda_s u\)

yielding

\[
(I + E^{-1}\Phi E^{-T}) v = (1 - \lambda_s) v
\]

with \( v = E^{-1}u \).

Hence \( \lambda_c = 1 - \lambda_s \), and since convergence is to a solution with \( |\lambda_s| < 1 \) and therefore \( \lambda_c < 1 \), \( C \) will be positive definite, and the solution represents a local minimum in Gibbs energy.

APPENDIX B: IMPLEMENTATION OF THE NEWTON-RAPHSON METHOD FOR TWO-PHASE PROBLEMS

The set of equations to be solved is

\[
f_i(K) = (\ln(v_i/V) + \ln \phi_i^R) - (\ln(l_i/L) + \ln \phi_i^L) = 0
\]
where \( v_i \) and \( l_i \) are the number of moles of component \( i \) in the vapour and liquid phase, respectively.

The Jacobian matrix is given by

\[
J_{ij} = \frac{\partial f_i}{\partial \ln K_j}
\]  

and the correction vector \( \beta \) with \( \beta_i = \Delta \ln K_i \) is found from

\[
J\beta = -f
\]  

The Jacobian matrix is calculated from

\[
J_{ij} = \frac{\partial f_i}{\partial \ln K_j} = \sum_i \frac{\partial f_i}{\partial l_m} \frac{\partial l_m}{\partial \ln K_j}
\]

yielding after some rearrangement

\[
J = BA^{-1}
\]

with

\[
B_{ij} = \frac{z_i}{x_i y_i} \delta_{ij} - 1 + \frac{V}{V + L} \left( \frac{\partial \ln \phi_i^V}{\partial n_j} + \frac{\partial \ln \phi_i^L}{\partial n_j} \right)
\]

and

\[
A_{ij} = \frac{z_i}{x_i y_i} \delta_{ij} - 1
\]

Since \( B \) is symmetric, we can use the decomposition

\[
B = LDL^T
\]

where \( L \) is unit lower triangular and \( D \) is diagonal with positive elements for a positive definite \( B \).

Then

\[
\beta = -AL^{-T}D^{-1}L^{-1}f
\]

where the cost of the decomposition and the subsequent back substitution is only about half of that required for conventional solution of eqn. (B3) by Gaussian elimination.

We may finally notice that the Jacobian \( J \) equals \( I - S \), see eqn. (A9). Hence, two eigenvalues of \( J \) are close to zero in the critical region.

APPENDIX C: CRITICAL POINTS ON MULTIPHASE BOUNDARIES

A critical point on a multiphase boundary is a point \((T_c, P_c)\) in the phase diagram where one of the equilibrium phases is critical. Here we shall briefly describe a method for direct calculation of a critical point on the three-phase boundary.

The two criticality conditions for a phase of composition \( x \) can be formulated in different ways (Peng and Robinson, 1977; Heidemann and
Khalil, 1980; Michelsen, 1980). The present derivation is based on the stability criterion used by Michelsen (1981a):

\[ g^*(Y) = 1 + \sum_i Y_i \{ \ln Y_i + \ln \phi_i(Y) - \ln x_i - \ln \phi_i(x) - 1 \} \geq 0 \]  

where the \( Y_i \) are mole number of a trial phase.

The gradient is given by

\[ \frac{\partial g^*}{\partial Y_i} = \ln Y_i + \ln \phi_i(Y) - \ln x_i - \ln \phi_i(x) \]  

and we note that \( g^*(x) = \frac{\partial g^*}{\partial Y}(x) = 0 \)

The system is unstable if the matrix of second derivatives has a negative eigenvalue at \( Y = x \). A zero eigenvalue corresponds to a point on the stability limit, and we obtain a critical point when the third derivative of \( g^* \) in the direction of the eigenvector corresponding to the zero eigenvalue is also zero.

Introducing new variables \( \alpha_i = 2(Y_i)^{1/2} \) yields

\[ B_{ij} = \left( \frac{\partial^2 g^*}{\partial \alpha_i \partial \alpha_j} \right)_{Y=x} = \delta_{ij} + (x_i x_j)^{1/2} \frac{\partial \ln \phi_i}{\partial n_j} \]  

Let the eigenvector of \( B \) corresponding to the smallest eigenvalue \( \lambda_{\text{min}} \) be \( u \)

\[ B u = \lambda_{\text{min}} u, \quad u^T u = 1 \]  

The first criticality condition is

\[ \lambda_{\text{min}}(T, P) = 0 \]  

Next define

\[ g^*(s) = g^*(\alpha) \]  

with

\[ \alpha_i = 2(x_i)^{1/2} + s \cdot u_i \]  

The second criticality condition is taken as

\[ (d^3 g^*/ds^3)|_{s=0} = 0 \]  

The third derivative is evaluated numerically as the second derivative of \( d g^*/ds \), where

\[ \frac{d g^*}{ds} = \sum_{i=1}^N \frac{\partial g^*}{\partial \alpha_i} \frac{d \alpha_i}{ds} = \sum_{i=1}^N u_i \frac{\partial g^*}{\partial \alpha_i} \]
A three point difference formula yields

\[
\left( \frac{d^3g^*}{ds^3} \right)_{s=0} = \frac{1}{\varepsilon^2} \left[ \frac{d}{ds} (s = -\varepsilon) - 2 \frac{d}{ds} (s = 0) + \frac{d}{ds} (s = \varepsilon) \right] + O(\varepsilon^2)
\]

\[
= \frac{1}{\varepsilon^2} \left[ \frac{d}{ds} (s = -\varepsilon) + \frac{d}{ds} (s = \varepsilon) \right]
\]

For the numerical evaluation, we take \(\varepsilon = 10^{-3}\).

Equations \(F_1(T, P, x) = \lambda_{\text{min}}(T, P, x) = 0\) and \(F_2(T, P, x) = (d^3g^*/ds^3)_{s=0}\) are solved numerically for \((T, P)\) by Newton–Raphson iteration, using numerical differentiation with respect to temperature and pressure. We use \(\Delta T = 10^{-4} \text{ K}, \Delta P = 10^{-4} \text{ atm}\). For critical points on the two-phase boundary the phase composition \(x\) is constant, but on multiphase boundaries \(x\) represents the composition of an equilibrium phase and hence depends on \(T\) and \(P\).

The points on the three-phase boundaries are calculated using the vapour–liquid flash procedure to obtain the composition of the equilibrium phases. The sensitivities of the phase compositions to the specified temperature and pressure, \(d/dT(x)\) and \(d/dP(x)\) are calculated from the Newton–Raphson solution, and the composition \(x + \Delta x\) at the perturbed conditions is simply taken as \(\Delta x = \Delta T \, d/dT(x)\) or \(\Delta x = \Delta P \, d/dP(x)\), respectively.

The computational requirements for evaluation of the criticality conditions and their temperature and pressure derivatives is modest, typically corresponding to two Newton–Raphson iterations for the flash calculation. Convergence is quadratic, but the initial estimates have to be very close.

**LIST OF SYMBOLS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B)</td>
<td>matrix of second derivatives of Gibbs energy</td>
</tr>
<tr>
<td>(F)</td>
<td>flash function, eqn. 3</td>
</tr>
<tr>
<td>(G)</td>
<td>Gibbs energy</td>
</tr>
<tr>
<td>(H_i)</td>
<td>see eqn. 11</td>
</tr>
<tr>
<td>(i, j)</td>
<td>component index</td>
</tr>
<tr>
<td>(J)</td>
<td>total number of phases</td>
</tr>
<tr>
<td>(K_i)</td>
<td>equilibrium factor, component (i)</td>
</tr>
<tr>
<td>(l, m, M, k, K)</td>
<td>phase index</td>
</tr>
<tr>
<td>(N)</td>
<td>number of components</td>
</tr>
<tr>
<td>(n_i)</td>
<td>mole number, component (i)</td>
</tr>
<tr>
<td>(P)</td>
<td>pressure</td>
</tr>
<tr>
<td>(R)</td>
<td>gas constant</td>
</tr>
<tr>
<td>(S)</td>
<td>matrix of partial derivatives, eqn. 6</td>
</tr>
</tbody>
</table>
\( t \) \hspace{1cm} \text{iteration number}
\( T \) \hspace{1cm} \text{temperature}
\( V \) \hspace{1cm} \text{vapour phase fraction}
\( V_m \) \hspace{1cm} \text{fraction of phase } m
\( x_i \) \hspace{1cm} \text{liquid phase mole fraction of component } i
\( y_i \) \hspace{1cm} \text{vapour phase mole fraction of component } i
\( y_{im} \) \hspace{1cm} \text{fraction of component } i \text{ in phase } m
\( z_i \) \hspace{1cm} \text{feed mole fraction of component } i
\( \delta_{ij} \) \hspace{1cm} \text{Kronecker delta function, } \delta_{ii} = 1, \delta_{ij} = 0, i \neq j
\( \lambda \) \hspace{1cm} \text{eigenvalue of } \Sigma
\( \phi_i \) \hspace{1cm} \text{fugacity coefficient of component } i
\( \phi_{im} \) \hspace{1cm} \text{fugacity coefficient of component } i \text{ in phase } m
\( \theta_{im} \) \hspace{1cm} \text{yield fraction, see eqn. 14}

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