A COMPUTATIONAL ALGORITHM FOR
VAPOR-LIQUID EQUILIBRIA
PHASE ENVELOPES

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For performing vapor-liquid equilibria phase envelope calculations, using equation of state models, several methods are available. However, most of these methods are either strongly dependent upon user-supplied initial estimates or are computationally slow. It has also been observed that these methods can occasionally converge to bubble-point solutions above the critical temperature or to dew-point solutions below it. The thermodynamic improbability of such solutions suggests that vapor-liquid equilibria calculation methods are unable to predict the critical point. Thus, the critical point must be determined by some other method.

The objective of my research has been to develop an algorithm to compute phase envelopes. Such an algorithm needs to be relatively free from the flaws mentioned above. This required a detailed study of the behavior of cubic equations of state, a better understanding of the thermodynamic critical point, a comparison of approximate and rigorous methods to calculate critical points, and an analysis of an acceleration technique to speed-up convergence of phase equilibria calculations.

The first two parts of this thesis deal with the study of phase equilibria calculations and critical point
estimation, respectively. In the third part, a phase envelope calculation method has been developed based upon the findings in the first two parts. This particular method generates complete phase envelopes without any user interaction.

In the course of my study, it was discovered that good techniques are available that lead to correct vapor-liquid equilibria solutions provided the final equations of state have turning points. However, when the equations of state do not have turning points, the solution becomes strongly dependent upon the initial estimates. As for the critical points, it was established that both, rigorous and approximate methods can fail depending upon the system or the initial estimates. The phase envelope generating algorithm developed herein has been successfully tested on many multicomponent mixtures with positive results. It is independent of user-supplied initial guesses, and has not led to a trivial solution in any of the test cases. Numerical difficulties with a particular accelerator were also encountered. Thus its use in the simulator is not recommended. A good test for false solutions has been proposed. When applied on several cases, it was observed that this test greatly reduces the incidence of false solution.
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CHAPTER I

INTRODUCTION

In an attempt to develop more efficient and robust methods to describe phase equilibria using cubic equations of state, work has been done to devise a new algorithm for vapor-liquid equilibria (VLE) phase envelope computations. Some of the flaws with robustness were seen to be due to an improper understanding of cubic equations of state (EOS), and thus a detailed analysis of the behavior of cubic equations has been carried out. Associated with this analysis is a discussion of a recently proposed criterion to ascertain the type of solution (i.e. vapor or liquid roots) obtained from cubic EOS's.

VLE calculations are known to become slow in the vicinity of the critical point. Major problems with convergence are also known to occur in this region. Thus, it is important to consider the merits of including in the phase envelope generating algorithm a method for determining the critical point of the system by either some approximate method or by a rigorous method. This necessitated a study of critical points of multicomponent systems which forms the second part of this thesis.

In order to improve the efficiency of VLE calculations,
an acceleration method was introduced into the algorithm and
tested for robustness, reduction in the number of
iterations, and an overall reduction of computation time.
Detailed analysis of the acceleration method is also
presented herein.

A robust phase envelope generation algorithm includes
the capability to change the type of equilibrium
calculation, to switch search directions, and to stop the
calculation. There are various ways to create such an
algorithm, and the algorithm developed is just one possible
example. The last portion of this work deals with the
details of this algorithm.

All three parts of this work, that is chapters 2, 3 and
4, are separate manuscripts. The first manuscript deals
with the development of a method to compute bubble-points or
dew-points of multicomponent mixtures. The second
manuscript compares rigorous and approximate methods of
determining critical points. The third manuscript presents
the details of the algorithm developed to construct complete
phase envelopes using the results of the first two
manuscripts.
CHAPTER II

CUBIC EQUATIONS OF STATE 1:
EQUILIBRIUM CALCULATIONS

Introduction

Accurate phase envelopes and a robust method for performing flash calculations are essential for determining the phase behavior of fluids and mixtures. A lot of work has been done in this area to accurately and efficiently predict the compositional behavior of multicomponent mixtures. The present work is concerned specifically with vapor-liquid equilibria. To model the equilibria, cubic equations of state have been used to predict the volumetric properties of both vapor and liquid phases as opposed to a split model which uses activity coefficients to predict liquid properties and fugacities to predict vapor properties.

There are three main advantages of using an equation of state model: (i) Higher accuracy of the model in predicting phase equilibria near the critical point, where the liquid phase behaves quite like the vapor phase; (ii) when the same equations are used to predict both phases, programming effort is reduced as compared to a split model; and (iii) the equation of state model is widely used in the industry.
Two parameter cubic equations of state are very convenient to use. They may not be as accurate as some of the more sophisticated equations, but the Soave modification of the Redlich-Kwong (SRK) and the Peng-Robinson (PR) equations of state are fairly accurate and relatively simple to use.

Some of the recent work which deals with the analysis of cubic equations of state includes that of Asselineau, et al. (1979) who elaborated on the likelihood of attaining a trivial solution at high pressures as a result of the equations of state having single real roots. However, they did not propose a reasonable method to judge the corresponding phase of the root of the cubic equation in the single real root region and used a complicated search procedure. Poling, et al. (1981) presented a method to determine the correct phase of a root based on an empirical relationship, but the approach is limited to relatively low pressures. Gundersen (1982) suggested the use of third order Newton's method for calculating roots of a cubic equation and proposed a good technique to forcibly assign a root to cubic equations that exhibited a particular shape in the single root region. Jovanovic and Paunovic (1984) presented a way to assign a correct root to a phase by perturbing the pressure during the initial iterations. This method is not useful if the calculations are performed at a fixed pressure. Veerana and Rihani (1984) also published details of the behavior of cubic equations within the three root region but did not provide a successful criterion in
the single root region. Rijkers and Heidemann (1985) carried out a very thorough analysis of trivial solutions and initial guesses. They concluded that the trivial solution could only be reached if calculations were performed outside the limit of mechanical stability. They also did not suggest a method for successfully avoiding the trivial solution at all points within the phase envelope.

This paper describes the nature of cubic equations of state with special reference to the SRK EOS, and methods of determining proper roots under different situations are analyzed. This is extremely important if convergence to a correct vapor-liquid equilibrium calculation is desired.

The SRK equation of state was used in this study although any other two parameter cubic equation of state could have been used without any difficulty.

Behavior of Cubic Equations

Solution of cubic equations is possible using two alternative procedures. The first one is an algebraic method which leads to three roots. Since this method also provides a means of obtaining complex roots, checks have to be included to ascertain the nature of the roots obtained. The second method involves the use of inverse trigonometric functions. The two methods are very similar. The trigonometric method, although less involved than the algebraic method, is not recommended since inverse trigonometric functions can be inaccurate in some computer
systems. Details of these methods are given in most mathematics handbooks such as the CRC Standard Mathematical Tables (Beyer, 1984).

An iterative solution of cubic equations is thus a viable alternative. With a properly selected initial guess and use of Newton's iterative technique, convergence of the cubic equation is monotonic and fast. Typically, using Newton's procedure and a reasonable tolerance, convergence is obtained in 3-6 iterations. The procedure for obtaining one root is given below:

For the cubic equation \( z^3 + Az^2 + Bz + C = 0 \), let

\[
F(z) = z^3 + Az^2 + Bz + C
\]  

then

\[
F'(z) = 3z^2 + 2Az + B
\]  

Initial guess on \( z = z_0 \)

\[
z_{i+1} = z_i - \frac{F(z_i)}{F'(z_i)}
\]  

Convergence is achieved when:

\[
\frac{|z_{i+1} - z_i|}{z_i} < \epsilon
\]

Where \( \epsilon \) is the tolerance.

Another proposed iterative procedure for solving cubic equations is an improvement upon the previous method and is called the third-order Newton's method (Gundersen, 1982). The algorithm is identical to that for the first-order method except that \( z \) is updated using a third-order correction term:
\[ z_{i+1} = z_i - \frac{F(z_i)}{F'(z_i)} \cdot \frac{2}{1 + \sqrt{1 - 2F''(z_i)F(z_i)/F'(z_i)^2}} \] (4)

where

\[ F''(z) = 6z + 2A. \] (5)

Both methods are prone to failure when \( F'(z) \to 0 \). In addition the third-order method also fails when:

\[ F''(z) \cdot F(z) / (F'(z))^2 > 0.5 \] (6)

When dealing with cubic equations of state, the third order method converges in 1 to 2 iterations less than the ordinary method. However, the increased computational cost per iteration and the additional check for failure do not really warrant its use in phase equilibria calculations.

At points where the first order method is expected to fail, i.e. \( F'(z) = 0 \), a robust algorithm should be designed to switch to the secant method, which though still not globally convergent, assures convergence provided the two initial steps are chosen carefully.

Before discussing the initiation criteria for converging on the appropriate root, it is necessary to discuss the possible shapes that a cubic equation can assume depending upon the coefficients \( A, B \) and \( C \). The forms of cubic equations with one or three real roots are shown in Figure 1 following the classification scheme of Gosset et al. (1986).

Form I has three real roots, whereas Forms II and III have only one real root even though they both have two
Figure 1. Shapes of Cubic Equations.
turning points. Forms IV and V have single real roots and no turning points. The difference in the last two shapes is slight but important as concerns the initial guess. For Form IV, the point of inflection lies in the region $F(z) > 0$; while for Form V, the point of infection is in the region $F(z) < 0$. Thus, it is necessary to know whether the cubic equation is of Type IV or Type V before an initial value can be assigned to $z$.

When the cubic equation has Form I its smallest root can always be obtained by initiating the procedure with values of $z$ lower than the smallest root. The largest root can similarly be obtained by giving an initial value of $z$ higher than the largest root. In dealing with the Equations of State (EOS's) the middle root is meaningless and need not be determined. For Types II and IV, the single root can be obtained using Newton's method by initiating at a low value of $z$. Similarly, for Types III and V, it is necessary to initiate the computation at a high value of $z$. This procedure of assigning initial values automatically prevents crossing a point where either $F'(z) = 0$ or $F''(z) = 0$. Thus all flaws of Newton's method are taken care of and convergence is guaranteed. However, due to machine restrictions a problem may arise with a cubic equation that has the shape shown in Figure 2.

In this particular curve there are three real roots. However, the higher two are coincident. When determining the larger root, $F'(z)$ may tend to zero. This may occur
Figure 2. Cubic Equation With Two Equal Roots.
earlier than \( F(z) \leq \) tolerance, particularly if the tolerance is chosen to be too small. There are two ways to circumvent this predicament: (i) by not setting a very small tolerance, and (ii) by forcing the algorithm to treat it as a curve of Type II. For the purpose of cubic EOS's a very precise value of \( z \) is not needed, and therefore choosing a modest tolerance never leads to a failure in convergence in all tested cases.

Now that a method for guaranteed convergence to the correct root has been established, a way to check the shape of the cubic equation must be determined. It is interesting to note that Equation 5 is a straight line with its root at \( z = A/3 \). This means that the point of inflection of the cubic is always given by:

\[
F''(z) = 0 \quad \text{at} \quad z = A/3
\]

(7)

Existence of the turning points of a cubic equation is readily obtained from the quadratic equation for \( F'(z) \), Equation 2. The turning points are real only when:

\[
A^2 \geq 3B
\]

(8)

If \( A^2 \geq 3B \), then the turning points can be obtained from the analytical solution of Equation 2:

\[
z_1, z_2 = \frac{-2A \pm \sqrt{4A^2 - 12B}}{6}; \quad (z_1 < z_2)
\]

(9)

Thus, the general procedure is to first obtain \( F(z) \) at \( z = A/3 \) to determine whether the inflection point is above
or below the line \( F(z) = 0 \). Then if \( A^2 < 3B \), the curve is of Type IV or Type V. If \( A^2 \geq 3B \), then \( z_1 \) and \( z_2 \) can be obtained from Equation 9, and \( F(z_1) \) and \( F(z_2) \) can be calculated. If \( F(z_1) < 0 \), then we have a Type III curve. If \( F(z_1) > 0 \), then we have a Type II curve. Otherwise the curve is of Type I. Figure 3 presents a flow-sheet of the root assignment procedure.

The Soave Redlich-Kwong Equation of State

The SRK EOS used in the equilibria calculation algorithm developed here is (Soave, 1972):

\[
P = \frac{(RT)}{(v-b)} - \frac{(a(T))}{(v (v + b))}
\]

where

\[
b_i = 0.8664 \frac{RT_i}{P_{ci}} \tag{11}
\]

\[
a(T)_{ii} = a(T_i) \alpha_{ii}(T_{r_i}, \omega_i) \tag{12}
\]

\[
a(T_i) = 0.42747 \frac{R^2 T_{ci}^2}{P_{ci}} \tag{13}
\]

\[
\alpha(T_{r_i}, \omega_i) = (1 + m_i (1 - T_{r_i}^{1/2}))^2 \tag{14}
\]

\[
m_i = 0.480 + 1.574 \omega_i - 0.176 \omega_i^2 \tag{15}
\]

\[
b = \sum z_i b_i \tag{16}
\]

\[
a = \sum z_i z_j a_{ij} (1 - k_{ij}) \tag{17}
\]

This equation is more conveniently used in the compressibility factor form:

\[
z^3 - z^2 + (A - B - B^2)z - AB = 0 \tag{18}
\]

where

\[
A = \frac{a(T)P}{R^2 T^2} \tag{19}
\]

\[
B = bP / RT \tag{20}
\]
Figure 3. Root Assignment Procedure.
Equation 18 is cubic in compressibility factor, \( z \), and the previously described procedure can readily be used to find the desired roots. The only reason for using \( z \) as opposed to volume (\( V \)) is that \( z \) varies within a much narrower domain. Thus it is safer to make initial guesses on \( z \) than on \( V \). With a good knowledge of the shape of the cubic EOS at a given pressure, \( P \), and temperature, \( T \), for a specific system, convergence is guaranteed to the correct root, if it exists, using either a volume or compressibility factor explicit EOS.

The coefficients \( A \) and \( B \) in the SRK EOS are functions of both \( P \) and \( T \). The functional behavior of \( A \) and \( B \) is very important when the phase envelope simulation is performed. Thus, before proceeding further in our discussion on the solution of the SRK, a brief treatment of the dependence of these coefficients on \( P \) and \( T \) is presented here.

Since \( b \) is independent of both \( T \) or \( P \), the relationship of \( B \) on \( T \) and \( P \) is straightforward:

\[
B \propto \frac{1}{T} \quad (21)
\]
\[
B \propto \frac{1}{P} \quad (22)
\]

However, the dependence of \( A \) on \( T \) is neither simple nor well behaved. Generally an approximate exponential decay of \( A \) with increasing \( T \) is observed. Thus, at low reduced temperatures \( A \) decreases sharply with increase in \( T \). The variation of \( A \) with \( T \) at higher reduced temperatures is negligible. The pressure dependence of \( A \) is the same as
that for B:

\[ A \propto P \]  \hspace{1cm} (23)

The dependence of these coefficients on pressure and temperature must be kept in view when phase equilibrium calculations are performed.

**Root Assignment Procedure**

To obtain the correct root of a cubic EOS it is essential to know whether a vapor root or a liquid root is desired. Referring to Figure 1, it is observed that when a Type I cubic equation is used, the lowest root gives the liquid \( z (z_L) \) and the highest the vapor \( z (z_v) \). Thus initiating the calculations with say \( z_0 = 0 \) leads to \( z_L \); if initial \( z_0 = 1 \) then \( z_v \) is obtained (Gundersen, 1982).

When a Type II EOS is used, \( z_L \) is computed in the usual manner. However, \( z_v \) does not exist, and any attempt to obtain \( z_v \) by setting \( z_0 = 1 \) will lead to either no convergence or \( z_L \). A similar difficulty is encountered when trying to obtain \( z_L \) from a Type III EOS. If a vapor root is desired in an EOS which exhibits a Type II form (i.e. only a liquid like root), then the minima in the curve is calculated. The value \( z_v \) is such that (see Figure 4) (Gundersen, 1982):

at \( z_v \), \( F(z_v) > 0 \), \( F'(z_v) = 0 \), \( F''(z_v) > 0 \)

The condition \( F(z_v) > 0 \) is satisfied automatically if the
Figure 4. Forcing a Root Assignment.
two derivatives are satisfied, because in a Type II equation the minima lies above $F(z) = 0$. A similar technique is used to assign a liquid-like root in an EOS of Type III:

at $z_L$, $F(z_L) < 0$, $F'(z_L) = 0$, $F''(z_L) < 0$

This method of assigning vapor-like roots to Type II and liquid-like roots to Type III cubic EOS's is useful during the initial iterations in a phase equilibria computation.

The only root obtained from cubic equations of Type IV or Type V may be either liquid or vapor type. There is no way to judge the phase of the compressibility factor root by observing the shape of the EOS when it has a shape of Type IV or Type V (Gosset, et al. 1986). For EOS's of Type IV or V other criteria have to be used to determine what kind of a root has been obtained. One such criterion is discussed later in this paper.

The complete algorithm for calculating the correct root in a cubic EOS is shown in Figure 5.

Avoiding False and Trivial Roots

In the course of phase equilibria calculations, sometimes a solution can be attained which satisfies the objective function, but is not the correct solution. This solution is usually obtained if the shape of the cubic EOS is not carefully analyzed and the initial estimate is far off from the final answer. Such a solution, commonly called a trivial solution, is indicated when all $K$-values are equal
Figure 5. Correct Root of a Cubic EOS.
to one. A false solution is obtained when the algorithm has converged to a VLE with one, or both cubic EOS's having roots assigned using Gundersen's technique. In other words, either the final liquid cubic EOS is of Type III, or the vapor cubic EOS is of Type II. For equilibria calculations, the proposed model employs cubic equations of state to simulate both the liquid and the vapor phases. A successful method for proper convergence on the cubic EOS has just been discussed. However, convergence of the cubic EOS does not always guarantee a solution to a bubble-point or dew-point calculation. In the following discussion a method is proposed to avoid cases leading to (i) no convergence, (ii) trivial solutions and (iii) false solutions. This method is very successful at low and moderate pressures. However, problems have been encountered at high pressures, especially in the retrograde region. A discussion of these problems is also presented herein.

When an EOS model is used for vapor-liquid equilibrium (VLE) calculations, it is important to note that two, not one, cubic equations are being used -- one for the vapor phase and one for the liquid phase. Each of these can have one or three real roots. Thus, we are dealing with a system where the cubic equations can exhibit a total of two, four, or six real roots. Analysis of the nature of these roots and subsequent proper selection and interpretation is the key to a successful VLE solution.

A pertinent question at this stage in the development
is whether there is any relationship between the number of roots and the location on the phase envelope with respect to the critical point, the cricondenbar, or the cricondentherm. There is no relationship. Details of the number of roots analysis are covered in a separate paper on critical points of mixtures (Aftab, 1987). For now it is sufficient to say that at the critical point the two cubic equations will be identical and will be of Type IV or Type V, depending upon whether the critical compressibility of the particular mixture is below or above 0.3333 (for the SRK).

The algorithm for calculating a bubble pressure at a specified temperature in its simplified form is shown in Figure 6. Initial estimates are required for P and K-values. Monotonic variations of coefficients A and B with respect to P assure that convergence on P is well behaved. Usually in the low pressure regions \( P_0 = 1 \text{ atm} \) is chosen as the initial guess (Gundersen, 1982). The initial guesses of the \( K_i \) are more critical. An empirical relationship such as the one proposed by Wilson (Rijkers and Heidemann, 1985) is fairly accurate for initializing the K-values for most mixtures at low pressures. As \( P_r \rightarrow 1 \), this type of a K-value estimation procedure becomes less reliable. Since the objective function is \( \Sigma y_i = 1 \); an inaccurate initial estimate of \( K_i \) can, and very frequently does, lead to the trivial solution as all \( K_i \rightarrow 1 \). At this condition all \( x_i = y_i \), thus making \( \Sigma y_i = 1 \). However, since convergence in the near critical region is desired, a positive means of
Figure 6. Computing Bubble-Pressure.
Figure 6 (continued).
differentiating between a trivial solution of all $K_i \rightarrow 1$ at a non-critical point and the true solution of all $K_i \rightarrow 1$ near the critical point has to be established.

Currently there are several phase envelope generators available which exhibit overlapping bubble-point and dew-point curves (Michelsen, 1980). A very likely reason for this behavior is explained below. When the necessary checks for overlapping bubble-point and dew-point curves are incorporated, the incidence of such a behavior is greatly reduced.

When a bubble-point curve goes past the critical point and either lies over the dew-point curve, curls into a van der Waals loop, or meanders meaninglessly, we have achieved a false convergence. False convergence is undesirable because it (i) gives us no indication of the critical point (although in most cases a near critical region can be estimated from the results), and (ii) it reduces the reliability of our results.

An analysis of the behavior of the VLE algorithm for predicting bubble points beyond the critical point on a system with a known critical point revealed that the objective function $\Sigma \chi_i - \Sigma \chi_i = 0$ is easily satisfied by performing a bubble-point calculation at points where the bubble-point curve should not exist. However, the final root obtained for the liquid compressibility from the cubic EOS was, very often, an assigned root. That is the final liquid cubic equation was of Type III. This assignment was
permitted only when the initial guess of $P$ or $T$ was far removed from the final expected converged solution. Therefore, in the proposed algorithm a check is included to determine when the objective function converges while either $z_L$ or $z_V$ does not exist and has been assigned a value to keep the algorithm from reaching a trivial solution during the initial iterations.

A point to be mentioned at this stage is that most algorithms that proceed past the critical point fail if the prediction happens to be at the critical point. This is because there is no provision to account for the true solution at the critical point when all $K_i \to 1$. It has been observed that on most systems the $K_i$ are far removed from one at small distances from the critical point and rapidly go to one as the critical point is approached.

Criterion of Poling, Grens and Prausnitz

The problem of trivial solution mentioned earlier can be rectified if a satisfactory method is obtained to check at each iteration if the compressibility factor root obtained is vapor-like or liquid-like. As discussed previously, with cubic equations of Types I to III, this is easy, and when the required root does not exist it is assigned a value by inspecting the turning points. However, for cubic equations of Type IV or Type V, this is no longer possible. A method that seems technically sound and feasible for incorporating in the algorithm is based on an
empirical criterion suggested by Poling, Grens and Prausnitz (1981). They determine the isothermal compressibility factor given by:

\[
\beta = \frac{1}{P} \cdot \left( 1 - \frac{1 - 2AB + zB + 2B^2z - Az}{z (3z^2 - 2z + A - B - B^2)} \right) \tag{24}
\]

They then use the following relationships to determine whether \(\beta\) is that for a liquid or vapor:

Liquid-like root if \(\beta < 0.005\)
Vapor-like root if \((0.9 / P) < \beta < (3 / P)\)

Since Type IV and V cubic equations are observed in the vicinity of the critical point, the inclusion of Poling's criterion can be used to go very close to the critical point without overshooting it. Thus, this seemingly allows a very good interpolation between the bubble-point and dew-point curves to give the critical point without ever needing to obtain it by a rigorous method. Unfortunately, Poling's criterion fails at high pressures and thus should not be used to predict phase equilibria at relatively high pressures.

This is not surprising. Depending upon the specified pressure, the criterion either has a large gap in which the \(\beta\) is neither liquid-like nor vapor-like, or the two ranges overlap. If the pressure exceeds 180 atm the ranges can be expected to overlap. At pressures greater than 600 atm the criterion becomes meaningless since all vapor-like \(\beta\)'s are necessarily also liquid-like. Another draw-back in this
criterion is that the liquid isothermal compressibility is always expected to be less than 0.005 atm. This is unlikely to be true all the time because liquid compressibility should also necessarily be a function of pressure. This discrepancy becomes apparent when predicting VLE at high pressures, which need not be in excess of 180 atm, as discussed in the results section.

A good criterion could be developed if a method is devised which predicts liquid compressibility well at high (especially super-critical) pressures. Work has been done on the Rackett EOS (Rackett, 1970) to give fairly accurate liquid phase densities below the critical point (Hankinson and Thomson, 1979; Thomson, et al., 1982). Extension of this work beyond the critical has not met with much success as yet. Therefore, this method was not included in the root assignment procedure.

Results

Figure 7 shows the phase envelope of a typical light hydrocarbon retrograde mixture (Rijkers and Heidemann, 1985) generated by using the equilibria computation technique developed in this study. For all test cases in this study all binary interaction parameters have been assumed to be zero. The thermodynamic data has been obtained from Reid, et al. (1977). The limits of the regions exhibiting different types of cubic equations are marked. In the regions where only Type IV and V cubic equations are
Figure 7. Phase Envelope of Mixture 1.
Figure 8. Phase Envelope of Mixture 2.
<table>
<thead>
<tr>
<th>Component</th>
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<th>Mixture 2</th>
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</tr>
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</table>
obtained, an accurate initial estimate of pressure was required to converge on specified temperatures. Similar behavior was also noted in other mixtures, such as the heavy oil shown in the phase envelope of Figure 8 (Whitson and Torp, 1983).

Figures 7 and 8 also show the regions where the criterion of Poling, et al. indicated that the compressibility factor root obtained was of the wrong type. If used in these equilibria calculations, Poling's criterion would have failed. Its failure in the case of Mixture 1 (compositions of both mixtures are given in Table I) occurs very close to the critical point, and thus it can be used at conditions a little removed from the critical region. However, in the case of Mixture 2, the criterion falters at points even far away from the critical region, clearly illustrating the limitations of this method of judging the nature of $z$ roots.

Conclusions

A very robust method has been developed for convergence to the correct root in all cases of Type I, II and III cubic EOS's. However, when Type IV or V cubic equations are encountered a correct root assignment cannot be guaranteed. The empirical criterion of Poling, et al. works reasonably well for Type IV and V cubic equations at low pressures, but fails when working with systems exhibiting a high cricondenbar. This implies that in most regions, an
equilibrium calculation can be performed without requiring an accurate initial estimate. For systems with large retrograde regions, or generally, for most mixtures near the critical point, Type IV or V cubic equations are observed. In such cases, accurate initial estimates may be necessary to prevent a trivial solution from being reached.
REFERENCES


CHAPTER III

CUBIC EQUATIONS OF STATE 2:
CRITICAL POINT ESTIMATION

Introduction

Phase envelope computations using equation of state (EOS) models have the disadvantage that an initial point for starting the envelope is not known. Thus several iterations may be necessary to establish the first converged point in the envelope. Another draw-back associated with such simulators is that a bubble-point or dew-point curve can sometimes be extended beyond the critical point, leading to the problem of false convergence. Even though false convergence can be easily tested and avoided (Aftab, 1987), this is a needless exercise and should, if possible, be avoided.

Knowledge of the vapor-liquid critical point of the system is thus a very desirable initial step in a vapor-liquid equilibria (VLE) phase envelope computation. It can provide a good starting point for bubble-point and dew-point curves or be used to overcome the problem of false convergence.

In this paper the critical point is defined and the similarities and differences with the mechanical critical
and the pseudocritical point, with which it is often confused, are enunciated. Methods to approximate and to rigorously calculate critical points using cubic equations of state are described briefly. The usefulness and limitations of these methods are also discussed in this paper.

Stability

A system in equilibrium does not undergo any change with time. However, a system in equilibrium need not be stable. (In this text stability and critical points without qualification refer to thermodynamic stability and thermodynamic critical points, respectively.) A system is said to be in a stable equilibrium state if any disturbance in the state is temporary, with the system finally returning to its original state. Conversely, if the equilibrium is unstable, any perturbation will have a permanent effect on the state of the system. Most real thermodynamic systems are usually in a metastable equilibrium state (Modell and Reid, 1983). This simply means that if the perturbations are outside a certain domain the effect will be permanent. If the disturbances are kept within a narrow range (here narrow is used in a relative sense), the system will revert back to its original state.

Thermodynamic stability in an isolated system is attained if it is allowed to reach a state of maximum entropy. For a non-isolated system the Fundamental Equation
can be used to express the criterion of entropy maximum as enthalpy minimum at constant entropy, pressure, and mass; Helmholtz energy minimum at constant temperature, volume, and mass; or Gibbs energy minimum at constant temperature, pressure, and mass. All these criteria are the same, and all are violated if the system becomes unstable. For pressure explicit equations of state, it is convenient to use the Helmholtz free energy minimization criterion (Modell and Reid, 1983).

A pure liquid when heated to its normal boiling point is expected to boil. However, if all nucleation sites are suppressed, the liquid can remain thermodynamically stable at an elevated temperature. As the temperature is increased a point is reached where spontaneous nucleation occurs and the liquid vaporizes. This point is known as the limit of intrinsic stability. Prior to attaining this limit, the phase may or may not have been stable. Nonetheless, it was stable before, and even at, the bubble-point. Thus the bubble-point and dew-point curves represent loci of points at which a phase, vapor or liquid, is inherently stable. However, the phase may continue to be stable beyond the phase boundary as explained above. It is intrinsically unstable when the limit of stability is crossed.

The above phenomenon is illustrated on a P-V diagram in Figure 1, which shows the behaviour of a true isotherm (i.e. one not generated by an equation of state). At point 'A' the bubble-point is reached. Stability can be maintained
Figure 1. Stability Limit.
beyond 'A' until point 'B' at which spontaneous nucleation takes place. At this point, for pure components, \( \left( \frac{\partial p}{\partial y} \right) = 0 \). Similarly point 'C' represents the dew-point and point 'D' the point below which the vapor phase becomes unstable.

When the locus of all points of stability limit is plotted, the dashed curve of Figure 1 is obtained. The limits of liquid and vapor stability approach each other, and for most systems, merge on the VLE curve at what is defined as the critical point. The critical point is thus a stable point at the limit of stability, since all points on the VLE curve are stable (Heidemann and Khalil, 1980).

The limit of stability curve happens to coincide with the \( \left( \frac{\partial p}{\partial y} \right) = 0 \) curve for a pure component. The curve \( \left( \frac{\partial p}{\partial y} \right) = 0 \) also represents the mechanical (as opposed to thermodynamic) stability of a system. This is because a system is clearly mechanically unstable if \( \left( \frac{\partial p}{\partial y} \right) > 0 \). When dealing with multicomponent systems, the limit of thermodynamic stability may be reached before the system becomes mechanically unstable. Thus the critical point, which can be shown to be where \( \left( \frac{\partial p}{\partial y} \right) = 0 \) and \( \left( \frac{\partial^2 p}{\partial y^2} \right) = 0 \) for a pure component, is generally not the critical point for mixtures. The critical point is always defined as a stable point at the limit of stability, whether it be for a single component or a mixture.
Critical Points

The nature of critical points can now be appreciated. A phase, say the liquid phase, is stable at the critical point. However, at this point spontaneous transformation to the vapor phase takes place. The vapor phase is also at its limit of stability and would similarly revert back to the liquid phase. In a real process this leaves us with indistinguishable phases. This can be related to the familiar experiment in which the meniscus disappears at the critical point. The following can be concluded about the critical point:

(i) At the critical point, the system is invariant (i.e. it has zero degrees of freedom).

(ii) Because there is no distinguishable characteristic between the two phases, they must be identical in every respect: fugacity, composition, density, compressibility, etc.

(iii) Since the stable system reaches the limit of stability only at the critical point, at points even slightly removed from the critical point the two phases are distinctly different. This implies that phase equilibria calculations, which cannot be modelled by cubic equations of state at the critical point, can be performed at points close to it.
Critical Point of a Pure Component

For a pure component the critical point is necessarily also the temperature and pressure maximum of the two phase boundary. The critical point of a pure component can be approximated by a cubic equation of state as shown in Figure 2. The cubic equation in the two phase region at temperature T exhibits three real roots, while the isotherm at temperature T lies in the single phase region and has only one real root. The critical isotherm at temperature T is on the VLE curve, and thus must have three real roots. However, at the critical point the two phases are identical, and the cubic equation must have three identical roots. As discussed earlier, the critical point of a pure component does coincide with the point at which \( \frac{\partial^2 P}{\partial V^2} = 0 \) and \( \frac{\partial^3 P}{\partial V^3} = 0 \) for a true isotherm. Thus it is not wrong to say that the equation of state for a single species predicts the critical point at which the first and second derivatives of pressure with respect to volume are both zero. This point represents the point of inflection which is coincident with the critical point of a pure component. With cubic equations of state, this point is constant as exhibited by such an equation of state expressed in the compressibility factor form:

\[
\begin{align*}
F(z) &= z^3 - z^2 + Qz - R \\
F'(z) &= 3z^2 - 2z + Q \\
F''(z) &= 6z - 2
\end{align*}
\]
Figure 2. Critical Point of a Pure Component.
Thus \( F(z) = 0, \ F'(z) = 0, \) and \( F''(z) = 0 \) have one unique solution at \( z = 1/3, \ Q = 1/3, \ R = 1/27. \) Hence, it is seen that the SRK predicts a critical compressibility factor \( z \) of \( 1/3 \) for all pure substances. The SRK is not accurate when it comes to predicting the critical point by using this method. In fact, no two parameter cubic equation of state is accurate in this respect, unless it is forced to fit the actual critical point, in which case it is not accurate for VLE predictions at points far from the critical point, which are usually of greater interest.

Calculation of Critical Points

The \( Z_c \) predicted by the SRK equation of state is often called the pseudocritical compressibility factor. The point at which this occurs is termed the pseudocritical point. The pseudocritical point has no physical significance except in the case of a pure component. It can be observed that \( Z_c \) is close to the actual critical compressibility of pure components because \( Z_c \) is the mechanical critical point, which, for a pure component, is identical to the thermodynamic critical point. For a mixture, the pseudocritical point predicted by the equation of state is the mechanical critical point for a pseudocomponent representing the entire mixture. This point is insignificant and calculating it serves no useful purpose in phase equilibria computations.

Many methods for the direct determination of critical
points are available. Recent work in the area of critical point determination can be attributed to Peng and Robinson (1977) who applied Gibbs' rigorous thermodynamic criterion to an equation of state to evaluate the critical point. Huron, et al. (1977) and Baker and Luks (1980) improved upon the initial guess method used by Peng and Robinson. Heidemann and Khalil (1980) chose to use Helmholtz energy minimization as the criterion for rigorously determining the critical point. Their algorithm reduced the computational effort a great deal. The method was robust and could handle systems with multiple or no critical points. Michelsen (1982) improved this method by simplifying the mathematics involved. The mathematics were further simplified for two parameter equations of state by Michelsen and Heidemann (1981). Michelsen (1984) carried his work further and, using a modified tangent plane criterion, proposed a new algorithm for which computational requirements are very modest. However, this particular method requires an initial estimate of the critical point, very close to its true value. Michelsen (1985) suitably expanded his algorithm for use with the generation of a phase envelope near the critical point. Here the method of Heidemann and Khalil will be described briefly (1980). This method was chosen because of its simplicity and reported robustness. Other recent methods use more sophisticated mathematical techniques to improve upon the above mentioned procedure (Billingsley and Lam, 1980, Michelsen, 1982, Michelsen,
Since the critical point is stable, the Helmholtz free energy with respect to adjacent points (within the limits of metastability) must be a minimum. Therefore, any perturbation of the system from the critical point must yield an increase in the Helmholtz free energy. This condition is combined with the criterion for a point to lie on the limit of thermodynamic stability.

The criterion for stability expressed in terms of Helmholtz free energy at constant temperature and volume is given by:

\[(A - A_o) - \sum_{i}^{N} \mu_i \Delta n_i / T_o, V_o > 0\] (4)

where \(\Delta n_i\) is any arbitrary change in mole fraction of the \(i\)-th component.

Expanding Equation 4 in Taylor series gives

\[\left[ A - A_o - \sum_{i}^{N} \mu_i \Delta n_i \right] = \frac{1}{2} \sum_{j}^{N} \left( \frac{\partial^2 A}{\partial n_i \partial n_j} \right) \Delta n_i \Delta n_j + \frac{1}{3} \sum_{k}^{N} \sum_{j}^{N} \left( \frac{\partial^3 A}{\partial n_i \partial n_j \partial n_k} \right) \Delta n_i \Delta n_j \Delta n_k + O(\Delta n^4)\] (5)

At the limit of stability, the quadratic term should be positive semi-definite, implying that a matrix 'Q' of elements \(q_{ij} = (\partial^2 A / \partial n_i \partial n_j)\) should have a zero determinant. To satisfy stability at this limit the cubic form must be zero. This is because if \(\Delta \tilde{n} = (\Delta n_i, \ldots, \Delta n_N)^T\) and \(Q \cdot \Delta \tilde{n} = 0\) then the first non-zero term in the Taylor series must be of even order.

\[C = \sum \sum \sum \left( \frac{\partial^3 A}{\partial n_i \partial n_j \partial n_k} \right) \Delta n_i \Delta n_j \Delta n_k = 0\] (6)
The above equation is solved simultaneously with $\text{Det}(Q) = 0$, where the $\Delta \vec{n}$ vector is obtained from $Q.\Delta \vec{n} = 0$.

This criterion is applied directly to the cubic EOS of interest to come up with a critical point for the system on the VLE curve predicted by the same EOS. The salient feature of combining such a method with a phase equilibrium algorithm is obvious -- it guides the algorithm in choosing the type of calculation, bubble-point or dew-point, in the correct domain. Also, this method can be used to calculate the critical point when a phase envelope is not desired.

Michelsen (1980) has presented a method particularly suited to VLE calculations, which avoids the need to actually calculate the critical point. He plots a bubble-point curve and an over-lapping dew-point curve. Then he finally plots the locus of a 50% flash. Extrapolation of this locus to the VLE curve (the phase envelope) gives the critical point as shown in Figure 3. Although this method is claimed to be extremely accurate, it cannot be used with algorithms that check and prevent a cross-over of bubble-point and dew-point curves (Figure 4).

Results

A computer program was developed based upon the method suggested by Heidemann and Khalil, and it has been tested on several mixtures. Good agreement with experimental critical points was observed in most cases such as the mixtures of Teja, et al. (1983) shown in Table I. However, this method
Figure 3. Michelsen's Approximation.
Figure 4. Situation Under Which Michelsen's Method Cannot be Used.
<table>
<thead>
<tr>
<th>Mixture</th>
<th>Experimental Tc(K), Pc(atm)</th>
<th>Predicted Tc(K), Pc(atm)</th>
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<td>Mixture 1</td>
<td>310.9 124.2</td>
<td>322.4 124.6</td>
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<tr>
<td>Mixture 2</td>
<td>387.1  71.1</td>
<td>396.0  69.3</td>
</tr>
<tr>
<td>Mixture 3</td>
<td>421.5  70.6</td>
<td>428.5  70.1</td>
</tr>
<tr>
<td>Mixture 4</td>
<td>256.1  108.9</td>
<td>291.2  114.7</td>
</tr>
</tbody>
</table>
did show convergence problems. Changing the Newton's method convergence of volume in the outer loop to the Secant or False-position methods improved the frequency of convergence. In some cases, convergence was also strongly dependent upon the initial estimate of volume as exhibited by Mixtures 3 and 4. When the initial volume was set at 4b, as recommended by Heidemann and Khalil, convergence could not be achieved with these two mixtures. The volume during the course of the iterations was observed to become negative. However, when the initial volume was set at about 3b, no numerical difficulty was encountered for these mixtures. This is because the cubic function is not well-behaved with respect to volume, and since negative volumes are not desired at any stage in the iterations, convergence cannot be guaranteed, even by a globally convergent method.

Michelsen's approximate method was also tested. Figure 5 shows a typical case where the 50% flash curve can be used (Friedemann, 1987). In some cases the 50% flash curve over-laps a portion of the VLE curve instead of intersecting it at one point. This further reduces the utility of this method to approximate critical points as is illustrated in Figure 6 by a typical oil mixture (compositions of all mixtures are given in Table II) (Friedemann, 1987). This problem can be overcome, somewhat, by plotting 20% flash or 80% flash curves instead of a 50% flash curve. In the case of mixtures of light gases with
Figure 5. Critical Point Approximation for Mixture 2.
<table>
<thead>
<tr>
<th>Comp.</th>
<th>Mixture 1</th>
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</table>
low concentrations of heavy hydrocarbons, for example, the 50% flash curve does lie close to the dew-point curve, whereas the 10% or 20% flash curve will provide a more accurate estimate of the phase boundary and an isochore.

Conclusions

The critical point is a point on the phase envelope where the properties of both phases become identical. If a critical point determination is required for phase envelope calculations then Michelsen's approximation technique can be used in most cases. In cases where the 50% isochore cannot be used, some other isochore can be used. The rigorous method of Heidemann and Khalil is susceptible to numerical errors. If the numerical problems are overcome, this method is suitable in applications where the complete phase envelope is not needed.
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CHAPTER IV

CUBIC EQUATIONS OF STATE 3: PHASE ENVELOPE CALCULATIONS

Introduction

In order to know the limits of the two phase region of a multicomponent mixture, phase envelope calculations are required. It is therefore necessary to have an algorithm that can accurately trace the phase envelope of a mixture within a temperature and pressure range. Such an algorithm must possess the capability of predicting the bubble-point and dew-point curves close to the critical point, and also be able to traverse the retrograde region, if the system exhibits one. Robustness of the algorithm is essential. The algorithm should be such that it does not have to rely on initial estimates by the user. In addition to that it should be able to generate the entire envelope without any user interaction. The method presented by Aftab (1987) to determine the correct root of a cubic equation of state (EOS) when it has real turning points, has been used to develop a simulator to perform vapor-liquid equilibria (VLE) phase envelope calculations. This simulator satisfies the requirements mentioned above.

There are three iterative loops in this algorithm: The
inner-most loop uses Newton's method to converge on compressibility factors (z). The next loop uses successive substitution to converge on K-values, which are updated by calculating fugacity coefficients from z's. The outer-most loop computes the correct pressure at a specified temperature by using finite-step Newton's method to optimize the summation of phase mole fractions.

This algorithm comprises three main parts which are discussed herein: (i) The initiation of a bubble-point or a dew-point calculation, (ii) a search method for the cricondentherm, and (iii) a set of criteria to terminate bubble-point or dew-point calculations.

Phase envelope calculations using this algorithm have been performed upon various multicomponent mixtures with positive results. This paper describes the details of the phase envelope computation technique. A discussion of the results obtained by testing it on several systems is also included.

Initiation

The proposed algorithm is a continuous phase envelope generator which requires no initial estimates by the user. The only information required is the lower limits of temperature and pressure below which the phase envelope is not desired, and the initial step-size on temperature. The best step-size is found by experiment for each system. Usually 5-50 K is good enough in most cases.
The lower limits of pressure and temperature must be low. This is because the initial guess on K-values is obtained by using Wilson's correlation (Rijkers and Heidemann, 1985), which is fairly accurate at low pressures but becomes very inaccurate at higher pressures. Also, convergence to the correct root is achieved with relative ease at lower pressures, because the root assignment method of Aftab (1987) guarantees a correct solution at lower pressures when the cubic equations have real turning points. A starting pressure of about 20 atm, or less, is recommended. The starting temperature should be such that the first converged point should not have a pressure much higher than the lower pressure limit.

The algorithm starts the phase envelope construction with bubble-point predictions. The lower temperature limit is used as the starting point. Once the initial bubble-point has been computed the algorithm uses the previous converged pressure as its initial pressure for the next temperature step. If convergence cannot be attained by this method, the step-size on temperature is reduced.

For the first dew-point, the procedure is slightly more involved. To avoid unnecessary calculations below the lower pressure limit, the lower pressure limit is chosen as the starting point, and using the Wilson equation (Rijkers and Heidemann, 1985) to estimate K-values, an approximate dew-temperature is obtained. This approximation is then
used as the specified temperature in the first dew-pressure calculation, as shown in Figure 1.

Change of Search Direction

In dealing with systems exhibiting retrograde regions a temperature maximum is encountered which may not be the critical point. This temperature maximum is almost always on the dew-point curve. When marching through such a region the temperature direction has to be changed. However, such an action may cause the algorithm to retrace the curve obtained to the cricondentherm. To prevent such a behavior it is necessary to have the algorithm change the temperature search direction without altering the pressure search direction.

A change in search direction is indicated when the algorithm oscillates while searching for a dew-pressure at a specified temperature, or when the K-value calculations fail to converge. In such a situation, the step-size is reduced. When the step-size goes below a specified limit, and the above mentioned behavior is encountered; the temperature search direction is reversed while the pressure search direction remains unchanged. If convergence is still not achieved then the calculation is terminated. Figure 2 shows a flow-chart of the method employed.
Figure 1. Initiation of the Dew-Point Curve.
Figure 1 (continued).
Figure 2. Change of Search Direction.
Termination Criteria

Bubble-point or dew-point calculations are terminated when the curve gets close to the critical point. When a bubble-point calculation is terminated the dew-point curve is commenced. When the dew-point computation is terminated the phase envelope is complete and the program stops execution.

The algorithm tests for the critical point by (i) observing if the temperature step size is too small, (ii) the number of iterations in the K-loop are too large, or (iii) a false solution to the cubic is being indicated in the z-loop (a case of overshooting the critical point without actually passing through it). Figures 3 and 4 show the termination criteria. In addition, a rigorous method for determining critical points, such as the one proposed by Heidemann and Khalil (Aftab, 1987), can be included in the package. This will help terminate the calculations when the bubble-point or dew-point curves try to cross the critical point.

It is rather difficult to set an absolute upper limit on the number of K-loop iterations to test nearing the critical region. Some systems are known to require a large number of K-loop iterations far away from the critical, particularly in the retrograde region. Thus, the best method at hand seems to be to record the number of K-loop iterations at the previously converged point and to abort the computation if the K-loop iterations exceed 1.1-5 times that for the previous point, depending upon the number of
Figure 3. Termination Criterion for Excessive K-Loop Iterations.
Figure 4. Termination Criterion for False Solution.
iterations required for the previous point.

Damping Predicted Pressures

At temperatures higher than the cricondentherm convergence cannot be achieved since the two-phase region clearly does not exist. However, the robust root finding algorithm used for solving the cubic equation of state still gives the liquid and vapor compressibilities. Thus fugacity coefficients can be computed and K-values can be updated. These K-values are meaningless and may or may not converge. In all but one test case the K-values did converge. When the K-values fail to converge the check for excessive K-loop iterations is triggered and the particular type of calculation in progress is terminated. But when K-values do converge the algorithm begins to oscillate as mentioned earlier. This necessarily induces large swings in the pressure predictions (see Figure 2). These pressure fluctuations can lead to numerical problems in subsequent calculations. Therefore, a damping of the pressure predictions is needed, and has been effectively incorporated in the algorithm.

Tolerances

Setting proper tolerances on the convergence of z, K-values, and pressure is very important. If the tolerance on z and K is too high an error in the final converged value is introduced. Too low a tolerance can, of course, lead to
unnecessary, time-consuming iterations. Thus the tolerances on $z$, $K$, and pressure are selected such that increasing them by an order of magnitude causes an error of 0.01 atm in the converged pressure.

In addition, a tolerance is also required for terminating the bubble-point or dew-point calculations, or for reversing the search direction. In most cases, this tolerance determines how close to the critical point the phase envelope can be calculated. However, phase equilibria calculations close to the critical point usually require a sharp increase in computer time. For most systems reasonable results are obtained with a tolerance of 0.1-0.2 K.

Acceleration

One of the slowest steps in a VLE computation is the updating of $K$-values. Generally the method of steepest descent is used (Heidemann, 1983). This is accomplished by obtaining the fugacity coefficients, $\hat{\phi}_i^\alpha$ of both liquid and vapor phases, where $\phi_i^\alpha$ is given by:

$$\phi_i^\alpha = \hat{f}_i^\alpha / P x_i^\alpha$$

where $i$ = $i$-th component
$\alpha$ = $\alpha$-phase
$\hat{f}_i^\alpha$ = component fugacity
$P$ = system pressure

At equilibrium
Starting with an initial K-value, fugacity coefficients are computed. K-values are then recalculated from the new estimates of the fugacity coefficients. This iterative procedure is then continued until the change in K-values becomes less than a specified tolerance, at which point the K-values are said to have converged.

This method usually works well except near the critical region. In such a region the number of iterations to converge on K-values rapidly increases. Slow convergence, in some systems, is also encountered near the retrograde region. In a bubble-point or dew-point prediction the hierarchy of nested iterations is indicated in Figure 5. Every evaluation of \( z \) can take as many as 5 iterations, giving as many as 10 iterations per K-loop. The requirement of two K-loops per P-loop iteration implies that there are as many as 20 inner-most loop iterations every time K-values are updated. Thus a couple of hundred K-loop iterations can drastically accentuate the computational costs. Hence an improved method for updating K-values is desirable.

Newton-Raphson convergence has met with mixed success when used to update K-values (Rijkers and Heidemann, 1985; Westman, et al., 1984). In most cases they observed a sharp reduction in the number of iterations. However, the most serious draw-backs were failure to converge at various
Figure 5. Heirarchy of Nested Loops.
points within the phase boundary, and time consuming matrix manipulations (Rijkers and Heidemann, 1985). For this reason Newton-Raphson convergence was not tested in this work since it was considered essential to have a robust simulation algorithm.

The study by Heidemann and Rijkers (1985) also revealed that a very useful method of accelerating convergence on K-values is by using a scalar acceleration factor coupled with the conventional successive substitution technique of Mehra, et al. (1983). Of course, computational costs per iteration are somewhat increased, but at the same time the number of iterations are reduced dramatically. Heidemann and Rijkers, however, did not mention the overall advantage in computational time achieved by using the accelerated successive substitution method.

Mehra, et al. (1983) made use of the similarity between successive substitution and method of steepest descent to come up with the accelerator used in this simulator:

\[ g_i = \partial(G/RT)/\partial n_{i2} = \ln f_{i2} - \ln f_{i1} = 0 \]  \hfill (5)

\[ K_i^{(k+1)} = K_i^{(k)} \left( f_i^L/f_i^V \right)^{(k)} \gamma^{(k)} \]  \hfill (6)

or,

\[ K_i^{(k+1)} = K_i^{(k)} \left( \phi_i^L/\phi_i^V \right)^{(k)} \frac{1}{K_i^{(k)}} \gamma^{(k)} \]  \hfill (7)

where,

\[ \gamma^{(k)} = \left| \begin{array}{c} \tilde{g}^{(k-1)T} \tilde{g}^{(k-1)} \\ \tilde{g}^{(k-1)T} \left( \tilde{g}^{(k)} - \tilde{g}^{(k-1)} \right) \end{array} \right| \]  \hfill (8)

and

\[ \gamma^{(0)} = \gamma^{(1)} = 1.0 \]  \hfill (9)
Thus using only a little more storage and computation, a Newton-like convergence is attained (Heidemann, 1983). However, it was observed that unless variations in K-values are bounded from iteration to iteration, sometimes divergence in K-values is obtained. Thus K-value variations required damping.

Results

The techniques developed in this paper have been tested on various systems, some of which are discussed here. Mixture 1 is a seven component hydrocarbon mixture used by Rijkers and Heidemann (1985) in their analysis of trivial solutions. It has been chosen because of the prominent retrograde region that it exhibits. Mixture 2 is a typical North Sea oil fraction, and has been used in order to check the behavior of the phase envelope calculation when the cricondenbar lies on the bubble-point curve. Mixture 3 is a wet gas which has an exaggerated retrograde region and a relatively low critical pressure. Mixture 4 is a three component system used by Gundersen (1982). Although this system has no retrograde region, it does display some unusual behavior near the critical point. Finally, Mixture 5 (Whitson and Torp, 1983) was selected because its composition is such that K-loop iterations increase sharply when the bubble-point curve traverses the critical point of methane. The compositions of all these mixtures are given in Table I.
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<thead>
<tr>
<th>Comp.</th>
<th>Mixture 1</th>
<th>Mixture 2</th>
<th>Mixture 3</th>
<th>Mixture 4</th>
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For most systems, gaps are observed between the bubble-point and dew-point curves. These gaps are a function of tolerance of temperature step-size, and thus are implementation dependent. Figures 6 and 7 show how the gap in the phase envelope of Mixture 1 can be closed by reducing the temperature tolerance from 0.2 K (Figure 6) to 0.1 K (Figure 7).

Figure 8 shows the phase envelope of Mixture 2. The algorithm had no difficulty in passing through the cricondenbar. From Figure 9, it is evident that for Mixture 5 the algorithm did not yield a complete phase envelope. This gap between the curves can be reduced by lowering the temperature tolerance, as mentioned above. However, this mixture takes too many iterations in the vicinity of the critical point to converge, and thus computations become extremely slow if the curves are extended beyond the points shown in Figure 9.

Despite various safe-guards built into this algorithm, Mixture 3 displayed an unusual behavior near the critical region, with the dew-point curve extending beyond the terminating point of the bubble-point curve (Figure 10). This could possibly be due to the failure of the EOS model used. Similarly, Mixture 4 behaved strangely in the critical region. Figure 11 is a magnified view of the kink in the bubble-point curve for this system. Again, the unexpected shape of the phase envelope is most probably due to the limitations of the SRK EOS.
Figure 6. Phase Envelope of Mixture 1
At a Tolerance of 0.2 K.
Figure 7. Phase Envelope of Mixture 1
At a Tolerance of 0.1 K.
Figure 8. Phase Envelope of Mixture 2.
Figure 9. Phase Envelope of Mixture 5.
Figure 10. Phase Envelope of Mixture 3.
Figure 11. Phase Envelope of Mixture 4.
The accelerating technique of Mehra, et al. was tested by measuring the computer time for various phase envelopes generated with, and without, the accelerator. It was observed that the accelerated procedure is indeed cost-efficient. Table II shows the CPU times required for various systems using the VAX 11/780 computer.

The most serious draw-back in this accelerator is shown in Figure 12. It has been seen that the accelerated successive substitution does not always converge to the local minima in Gibbs' Energy. Thus a very narrow step-size has to be used in order to expect convergence to the correct solution. Generally, a correct convergence is attained if the initial guess of pressure is lower than the final converged pressure. Therefore, the accelerated version is liable to fail when marching down in pressures in the retrograde region, and thus its use is not recommended.

Further Suggestions

Table III shows the actual output for a phase envelope calculation using mixture 1. The two most noticeable things are: (i) the sharp increase in the number of K-loop iterations as the calculations progress, and (ii) the gradual reduction in temperature step-size as the critical point is approached. In the critical region the algorithm is dealing with cubic equations which have no real turning points (Aftab, 1987). Therefore, convergence to the correct root can only be achieved if the initial estimate of
### TABLE II

EFFECT OF ACCELERATION

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<th>System</th>
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Figure 12. Failure of Acceleration (Mixture 1).


**TABLE III**

**PHASE ENVELOPE CALCULATIONS**

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pressure is close to the final value. This algorithm uses successive substitution on pressures, and thus a reduction in step-size is necessary to assure convergence in the pressure loop. A method which fits a spline to the previously converged points and extrapolates it to give the initial estimate for the next point would be useful in avoiding this reduction in step-size, and thus lower the computational costs in the region where convergence requires a lot of iterations.

Conclusions

An algorithm to accurately simulate phase envelopes of multicomponent mixtures has been developed and successfully tested on a number of systems. This algorithm is self-starting and is capable of accurately tracing both bubble-point and dew-point curves without any interaction by the user. Near the critical point the step-size on temperature is automatically reduced and the progress of the curve slows down. However, convergence has been obtained on all tested cases even in this region.
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