A COMPUTATIONAL ALGORITHM FOR

VAPOR-LIQUID EQUILIBRIA

PHASE ENVELOPES

By

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Bachelor of Science

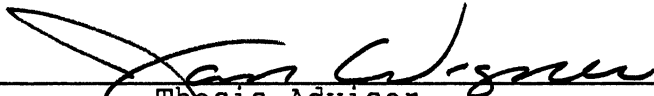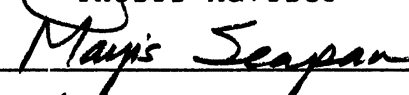University of the Punjab

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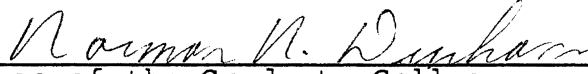
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PREFACE

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 intial 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.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

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

$$F(z) = z^3 + Az^2 + Bz + C \tag{1}$$

then

$$F'(z) = 3z^2 + 2Az + B \tag{2}$$

Initial guess on $z = z_0$

$$z_{i+1} = z_i - F(z_i) / F'(z_i) \tag{3}$$

Convergence is achieved when: $\left| \dfrac{z_{i+1} - z_i}{z_i} \right| < \epsilon$

Where ϵ 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:

$$z_{i+1} = z_i - \frac{F(z_i)}{F'(z_i)} \cdot \frac{2}{1 + \sqrt{(1 - 2F''(z_i) \cdot F(z_i)/F'(z_i)^2)}} \qquad (4)$$

where

$$F''(z) = 6z + 2A. \qquad (5)$$

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

$$F''(z) \cdot F(z) / (F'(z))^2 > 0.5 \qquad (6)$$

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
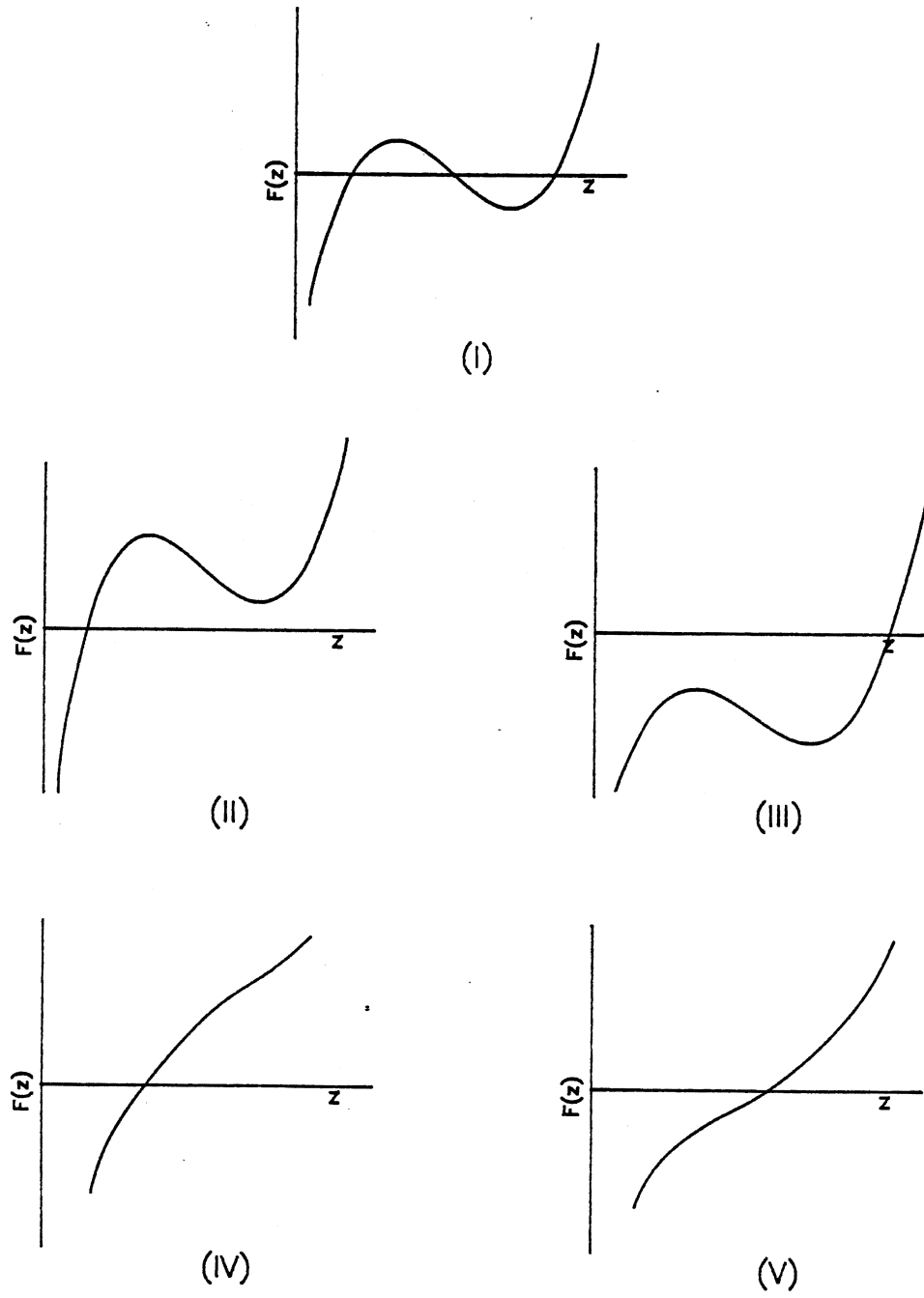
Figure 1. Shapes of Cubic Equations.

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
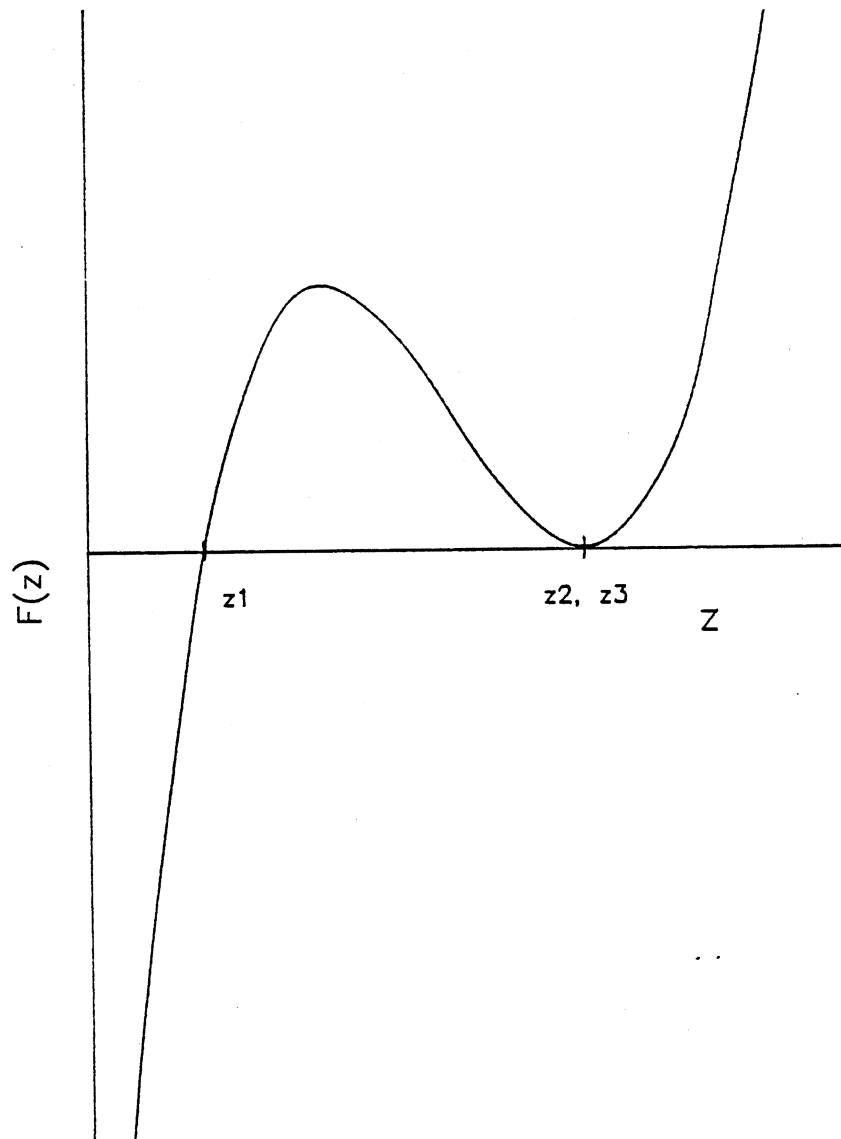
Figure 2. Cubic Equation With Two
Equal Roots.

earlier than F(z) <= 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:

$$F''(z) = 0 \quad \text{at} \quad z = A/3 \tag{7}$$

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:

$$A^2 \geqslant 3B \tag{8}$$

If $A^2 >= 3B$, then the turning points can be obtained from the analytical solution of Equation 2:

$$z_1, z_2 = \frac{-2A \pm \sqrt{4A^2 - 12B}}{6} \quad ; \quad (z_1 \leqslant z_2) \tag{9}$$

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 $A^2 >= 3B$, 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 $F(z_2) > 0$, 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):

$$P = (RT / (v-b)) - (a(T) / (v (v + b))) \tag{10}$$

where

$$b_i = 0.8664 \, RT_{c_i} / P_{c_i} \tag{11}$$

$$a(T)_{ii} = a(T_{c_i}) \, \alpha_{ii}(T_{r_i}, \omega_i) \tag{12}$$

$$a(T_{c_i}) = 0.42747 \, R^2 T_{c_i}{}^2 / P_{c_i} \tag{13}$$

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

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

$$b = \Sigma z_i b_i \tag{16}$$

$$a = \Sigma\Sigma z_i z_j \cdot a_{ij} (1 - k_{ij}) \tag{17}$$

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

$$A = a(T)P / R^2 T^2 \tag{19}$$

$$B = bP / RT \tag{20}$$

Start

Input parameters of cubic

Obtain z_M at $F'(z)=0$

$A^2 < 3B$? — N → Obtain z_1, z_2 roots of $F'(z)=0$

Y

$F(z_M) < 0$? — Y → Cubic of type (IV) → B

N

Cubic of type (V)

A →

$F(z_1) < 0$? — Y → Cubic of type (III) → A

N

$F(z_2) > 0$? — Y → Cubic of type (II)

N

Cubic of type (I)

Higher root desired? — Y →

N

z_0 is high

z_0 is low

B

Newton's convergence on z's

Print z

Stop
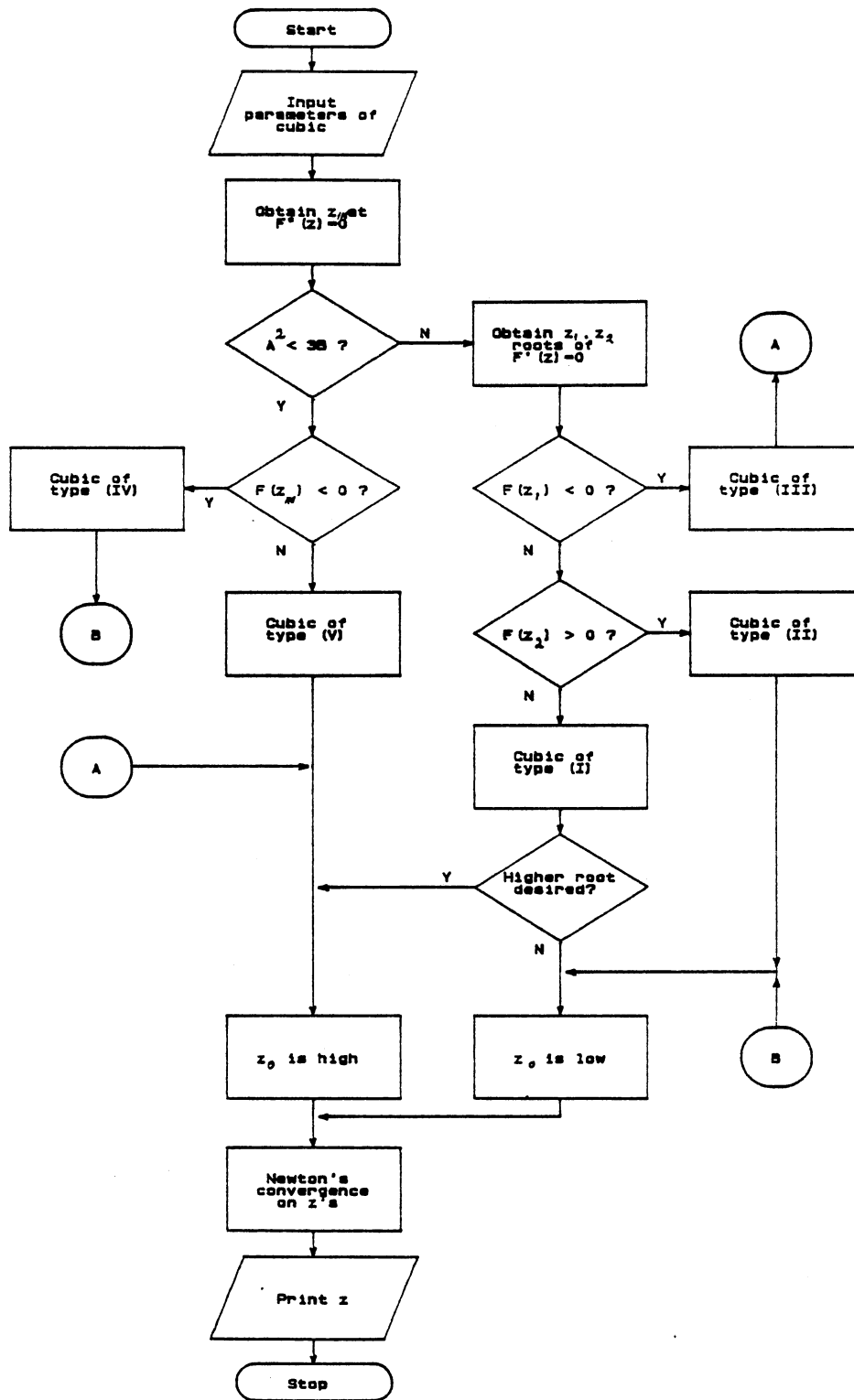
Figure 3. Root Assignment Procedure.

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:

$$B \propto P \tag{21}$$

$$B \propto 1 \, / \, T \tag{22}$$

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:

$$A \propto P \qquad\qquad (23)$$

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 $z_o = 0$ leads to z_L; if initial $z_o = 1$ 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 $z_o = 1$ 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
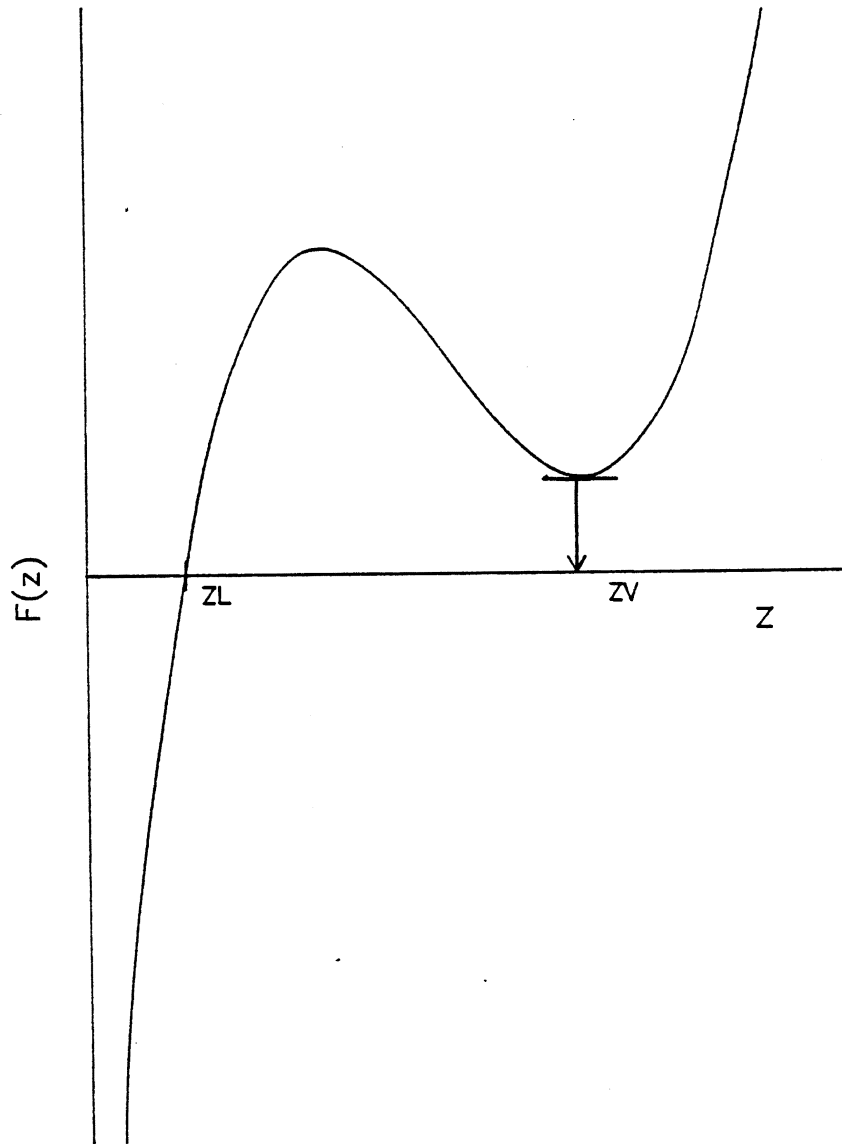
Figure 4.   Forcing a Root Assignment.

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
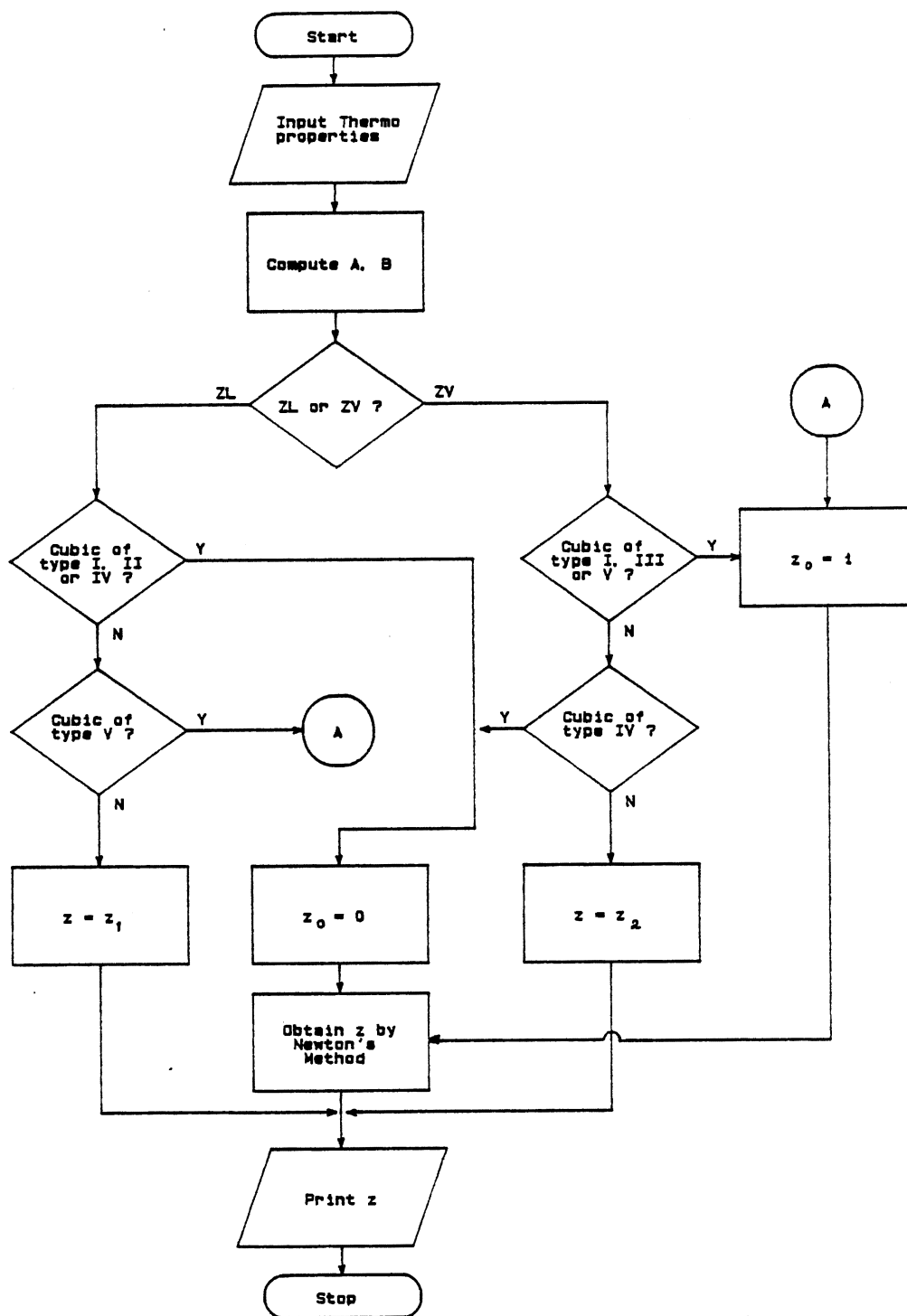
Figure 5. Correct Root of a Cubic EOS.

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 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 --> 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 --> 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
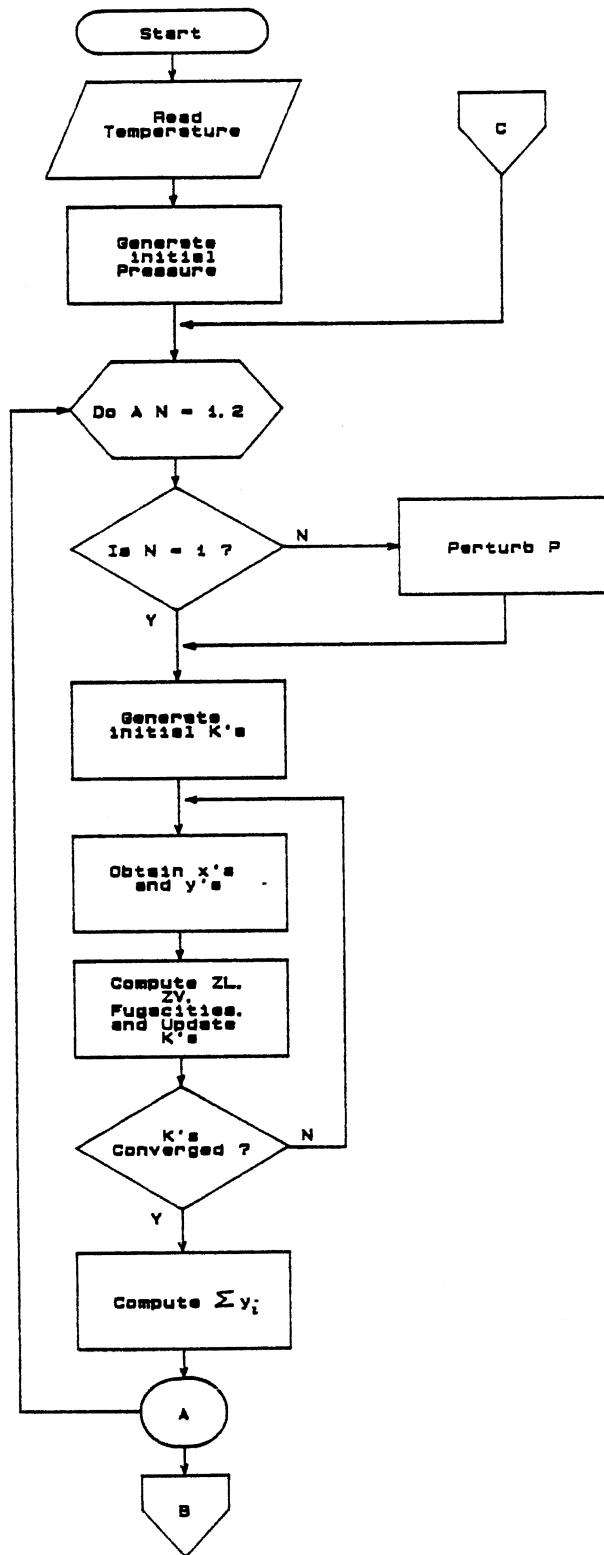
Figure 6. Computing Bubble-
Pressure.
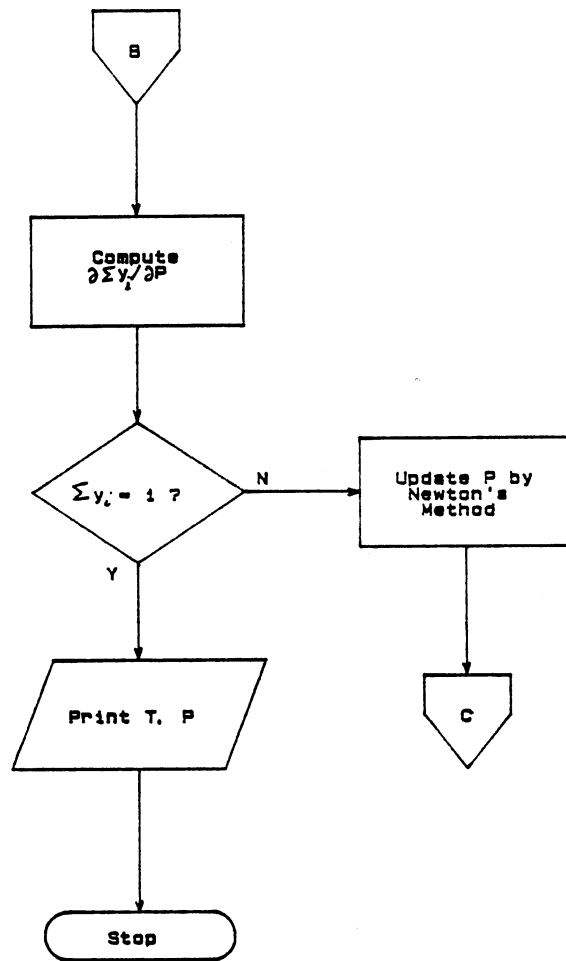
Figure 6 (continued).

differentiating between a trivial solution of all $K_i \longrightarrow 1$
at a non-critical point and the true solution of all
$K_i \longrightarrow 1$ 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 $\Sigma x_i - \Sigma y_i = 0$ 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 $K_i \dashrightarrow 1$. 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:

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

They then use the following relationships to determine whether β 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 β 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 β'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

Region	L-EOS Type	V-EOS Type	Poling's Criterion
A	2	1	OK
B	4	1	OK
C	4	5	OK
D	4	5	Failed
E	4	1	OK
F	4	3	OK
G	4	5	OK

Figure 7. Phase Envelope of Mixture 1.

Region	L-EOS Type	V-EOS Type	Poling's Criterion
A	4	1	OK
B	4	4	Failed
C	5	5	Failed
D	4	1	OK
E	5	1	OK
F	5	3	Failed
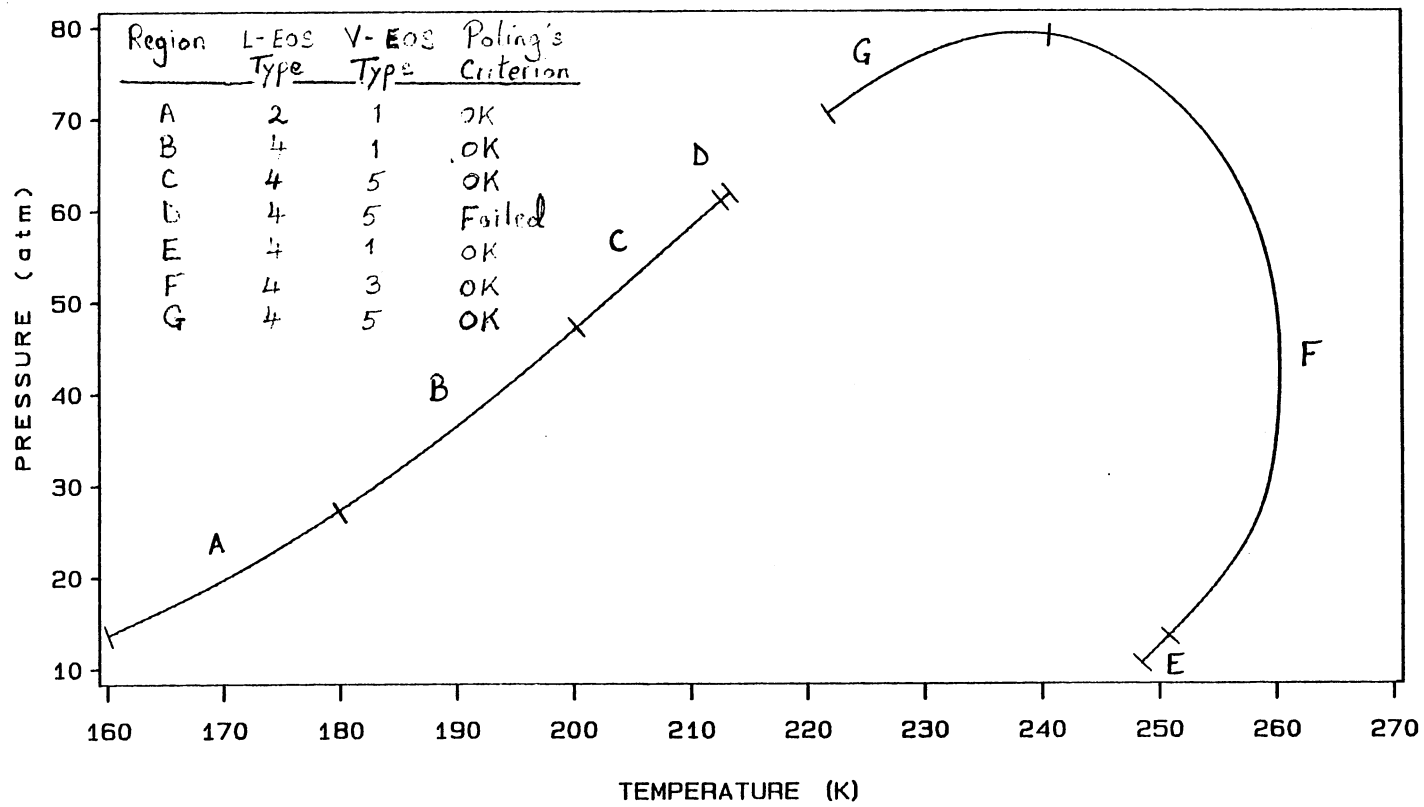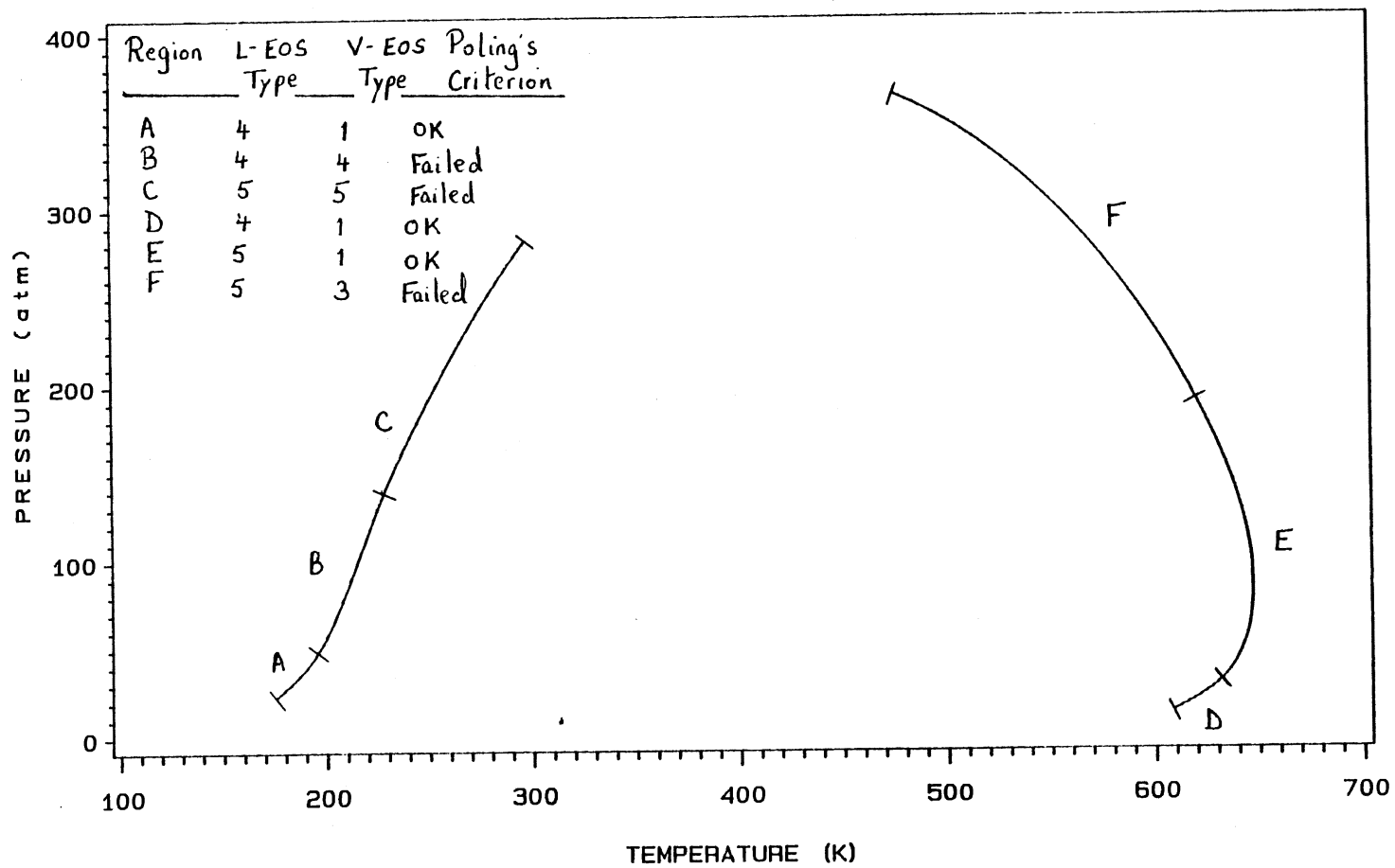
Figure 8.   Phase Envelope of Mixture 2.

TABLE I

COMPOSITIONS OF MIXTURES

Component	Mixture 1	Mixture 2
CO_2	.1000	.0237
N_2	–	.0031
C1	.8608	.7319
C2	.0247	.0780
C3	.0067	.0355
i–C4	–	.0071
n–C4	.0045	.0145
i–C5	–	.0064
n–C5	.0024	.0068
n–C6	.0009	.0109
Frac 1	–	.0325
Frac 2	–	.0214
Frac 3	–	.0114
Frac 4	–	.0098
Frac 5	–	.0071

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

Aftab, T., "A Computational Algorithm for Vapor-Liquid Equilibria Phase Envelopes." M.S. Thesis, Oklahoma State University, Stillwater, 1987.

Anderson, T.F. and Prausnitz, J.M., "Computational Methods for High-Pressure Phase Equilibria and Other Fluid-Phase Properties Using a Partition Function. 2. Mixtures." Ind. Eng. Chem. Process Des. Dev., 19 (1980), 9-14.

Asselineau, L., Bogdanic, G. and Vidal, J., "A Versatile Algorithm for Calculating Vapor-Liquid Equilibria." Fluid Phase Equil., 3 (1979), 273-290.

Beyer, W.H. (editor), "Standard Mathematical Tables", 27th edition, 1984. The CRC Press: 9-11.

Gosset, R., Heyen, G. and Kalitventzeff, B., "An Efficient Algorithm to Solve Cubic Equations of State." Fluid Phase Equil., 25 (1986), 51-64.

Gundersen, T., "Numerical Aspects of the Implementation of Cubic Equations of State in Flash Calculation Routines." Comp. and Chem. Eng., vol. 6, no. 3 (1982), 245-255.

Hankinson, R.W. and Thomson, G.H., "Calculating Liquid Densities Accurately." Hydrocarbon Processing, Sept. 1979, 277-283.

Jovanovic, S. and Paunovic, R., "Generating Appropriate Density Values From Cubic State Equations to Avoid False Unit K Values. Application to Distillation Problems." Ind. Eng. Chem. Process Des. Dev. (1984) 23, 801-805.

Michelsen, M.L., "Calculation of Phase Envelopes and Critical Points for Multicomponent Mixtures." Fluid Phase Equil., 4 (1980), 1-10.

Poling, B.E., Grens II, E.A. and Prausnitz, J.M.,
    "Thermodynamic Properties from a Cubic Equation of
    State: Avoiding Trivial Roots and Spurious
    Derivatives." Ind. Eng. Chem. Process Des. Dev., 20
    (1981), 127-130.

Reid, R.C., Prausnitz, J.M. and Sherwood, T.K., "The
    Properties of Gases and Liquids", 3rd edition (1977),
    McGraw-Hill Book Company.

Rackett, H.G., "Equation of State for Saturated Liquids."
    J. of Chem. and Eng. Data, vol. 15, no. 4 (1970),
    514-517.

Rijkers, M.P.W. and Heidemann, R.A., "Convergence Behavior
    of Single Stage Flash Calculations." Amer. Chem. Soc.
    Symposium on "Equations of State - Theory and
    Applications", Miami Beach, Florida, April 28 - May 3,
    1985.

Soave, G., "Equilibrium Constants from a Modified
    Redlich-Kwong Equation of State." Chem. Eng. Sci., 27
    (1972), 1197-1203.

Thomson, G.H., Brobst, K.R. and Hankinson, R.W., "An
    Improved Correlation for Densities of Compressed
    Liquids and Liquid Mixtures." AIChE J., vol. 28, no. 4
    (1982), 671-676.

Veerana, D. and Rihani, D.N., "Avoiding Convergence
    Problems in VLE Predictions Using an Equation of
    State." Fluid Phase Equil., 16 (1984), 41-55.

Whitson, C.H. and Torp, S.B., "Evaluating Constant-Volume
    Depletion Data." J. of Pet. Technology, March 1983,
    610-620.

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
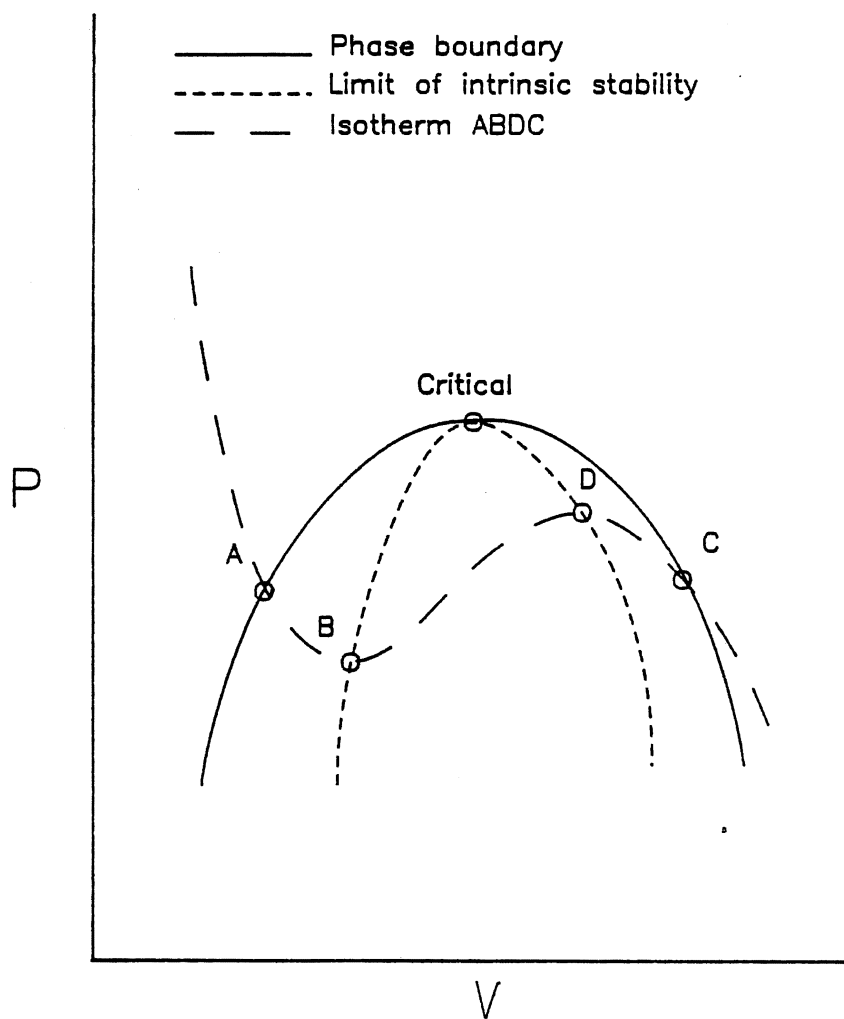
Figure 1. Stability Limit.

beyond 'A' until point 'B' at which spontaneous nucleation takes place. At this point, for pure components, $\left(\frac{\partial P}{\partial V}\right) = 0$. 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 $\left(\frac{\partial P}{\partial V}\right) = 0$ curve for a pure component. The curve $\left(\frac{\partial P}{\partial V}\right) = 0$ also represents the mechanical (as opposed to thermodynamic) stability of a system. This is because a system is clearly mechanically unstable if $\left(\frac{\partial P}{\partial V}\right) > 0$. 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 $\left(\frac{\partial P}{\partial V}\right) = 0$ and $\left(\frac{\partial^2 P}{\partial V^2}\right) = 0$ 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 $\left(\dfrac{\partial P}{\partial V}\right) = 0$ and $\left(\dfrac{\partial^2 P}{\partial V^2}\right) = 0$ 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:

$$F(z) = z^3 - z^2 + Qz - R \tag{1}$$

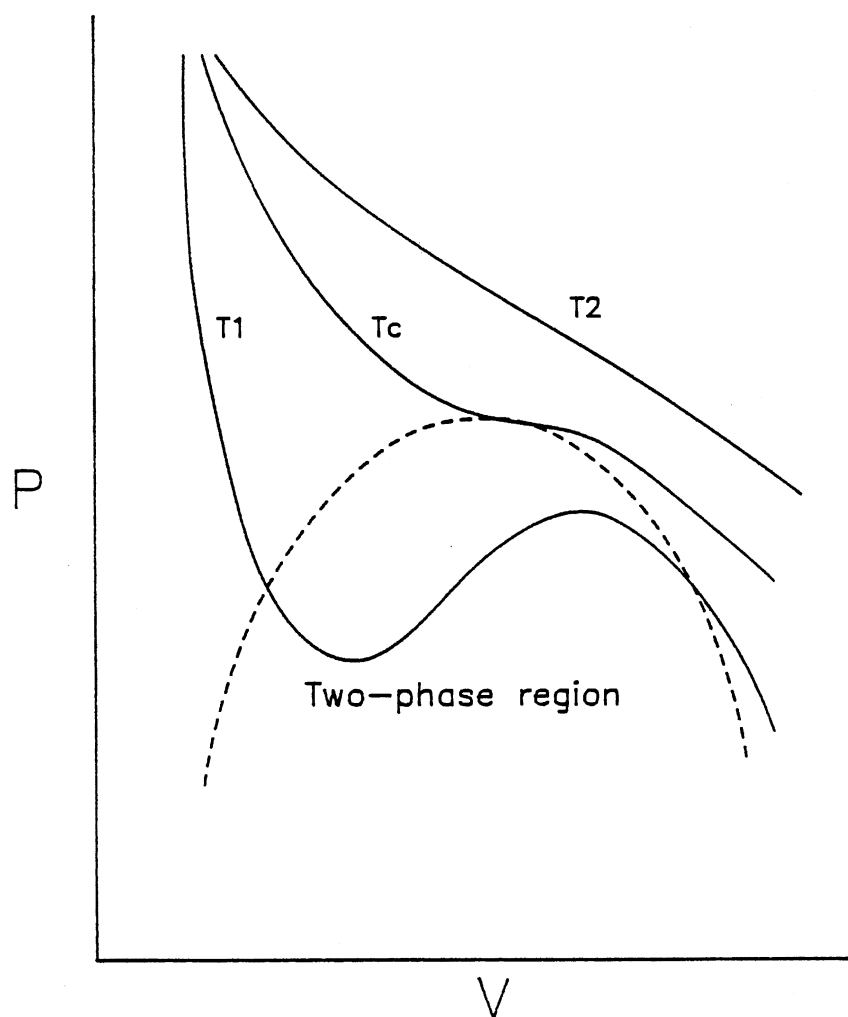$$F'(z) = 3z^2 - 2z + Q \tag{2}$$

$$F''(z) = 6z - 2 \tag{3}$$

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,

1984).

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:

$$\left((A - A_0) - \sum_i^N \mu_{io}\Delta n_i\right)_{T_o,V_o} > 0 \tag{4}$$

where Δn_i is any arbitrary change in mole fraction of the i-th component.

Expanding Equation 4 in Taylor series gives

$$\left[A - A_0 - \sum_i \mu_{io}\Delta n_i\right]_{T_o,V_o} = 1/2! \sum_j \sum_i (\partial^2 A/\partial n_i \partial n_j)\Delta n_i \Delta n_j +$$

$$1/3! \sum_k \sum_j \sum_i (\partial^3 A/\partial n_i \partial n_j \partial n_k)\Delta n_i \Delta n_j \Delta n_k + O(\Delta n^4) \tag{5}$$

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 $\Delta \bar{n} = (\Delta n_1, ..., \Delta n_N)^T$ and $Q.\Delta \bar{n} = 0$ then the first non-zero term in the Taylor series must be of even order.

$$C = \sum\sum\sum \left(\frac{\partial^3 A}{\partial n_i \partial n_j \partial n_k}\right) \Delta n_i \Delta n_j \Delta n_k = 0 \tag{6}$$

The above equation is solved simultaneously with Det(Q) = 0, where the $\Delta\bar{n}$ vector is obtained from $Q.\Delta\bar{n}$ = 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
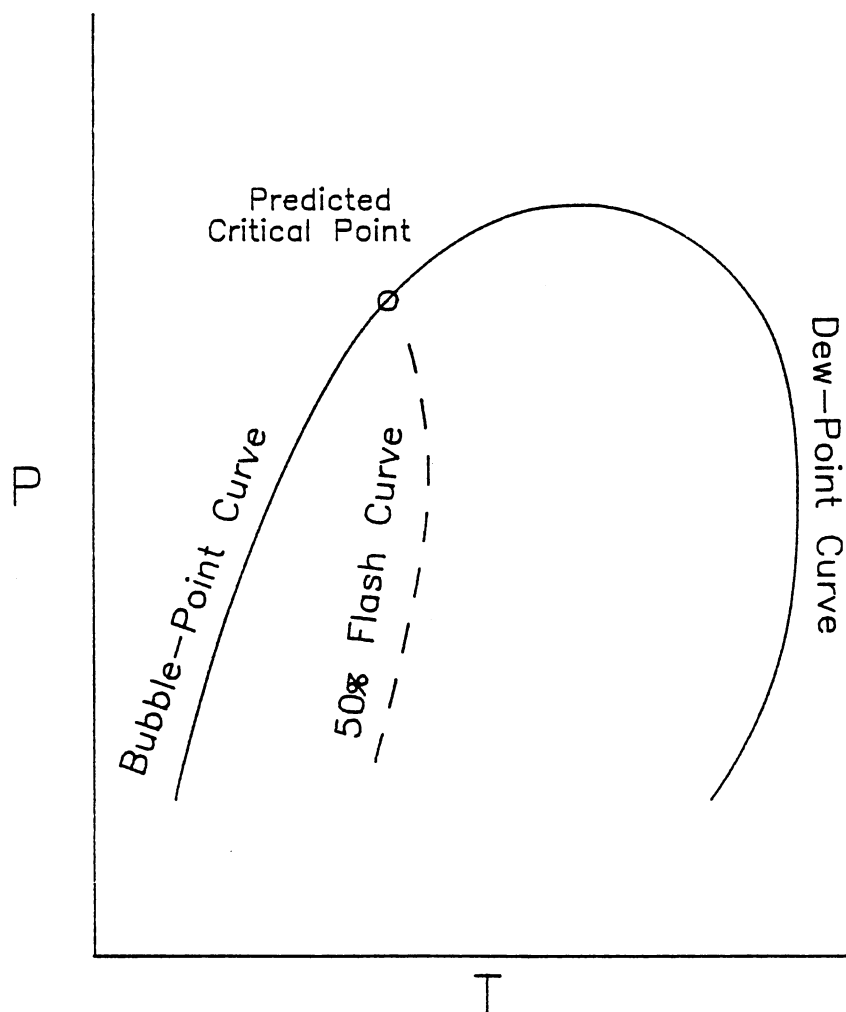
Figure 3.   Michelsen's Approximation.
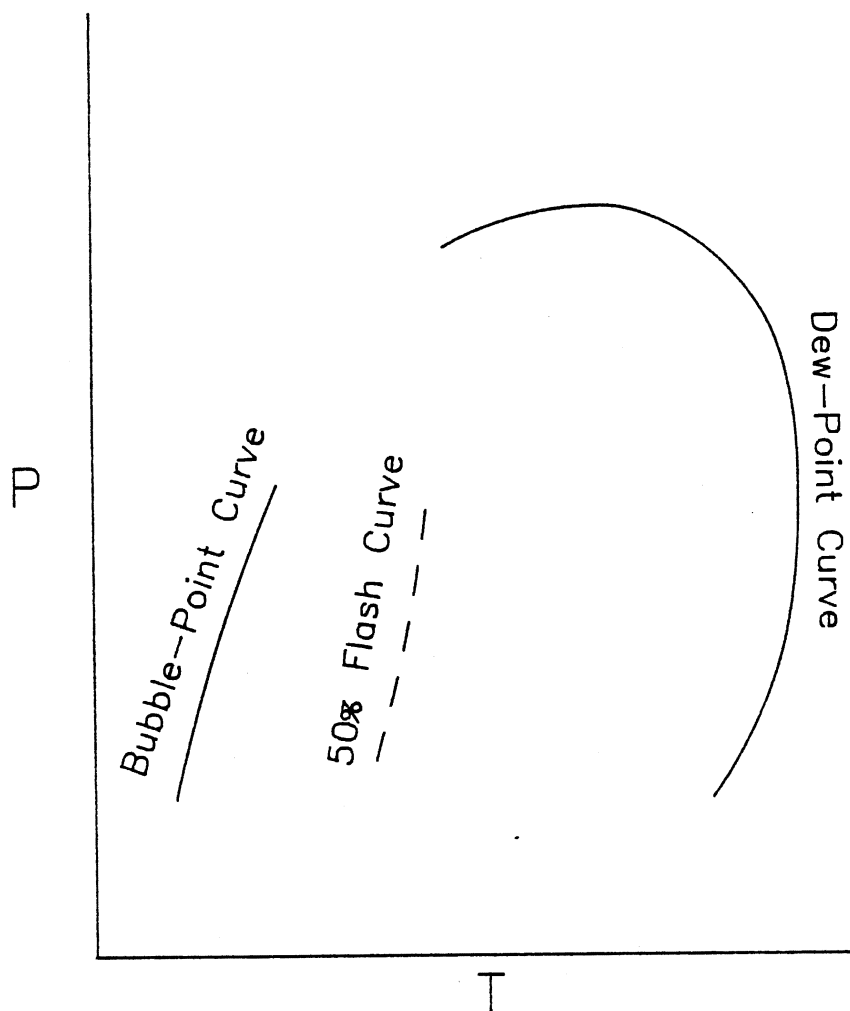
Figure 4.   Situation Under Which
             Michelsen's Method
             Cannot be Used.

TABLE I

COMPARISON OF EXPERIMENTAL AND PREDICTED
CRITICAL POINTS

Mixture	Experimental Tc(K), Pc(atm)		Predicted Tc(K), Pc(atm)	
Mixture 1	310.9	124.2	322.4	124.6
Mixture 2	387.1	71.1	396.0	69.3
Mixture 3	421.5	70.6	428.5	70.1
Mixture 4	256.1	108.9	291.2	114.7

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 exihibited 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 (compostions 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
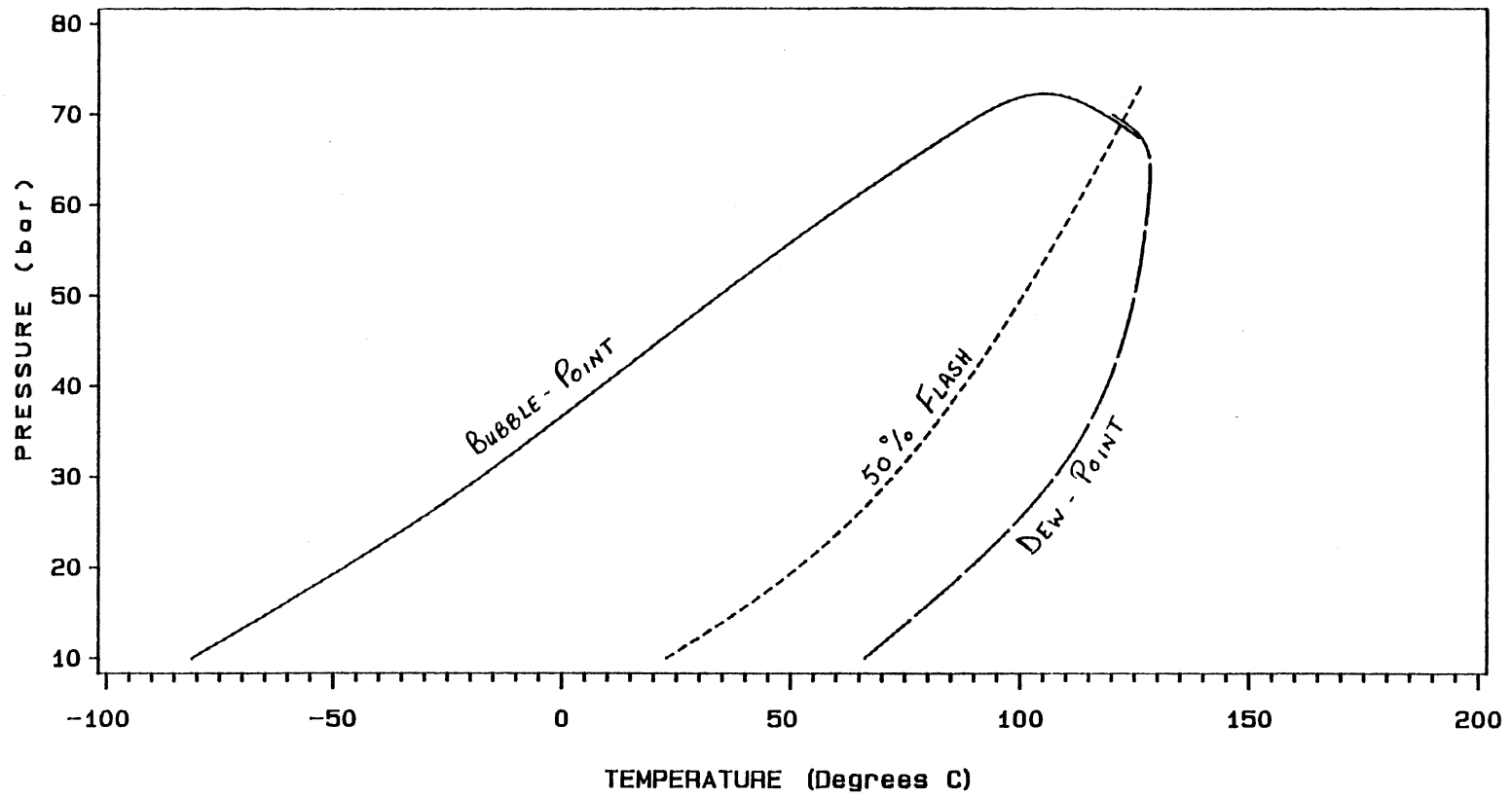
Figure 5. Critical Point Approximation for Mixture 2.
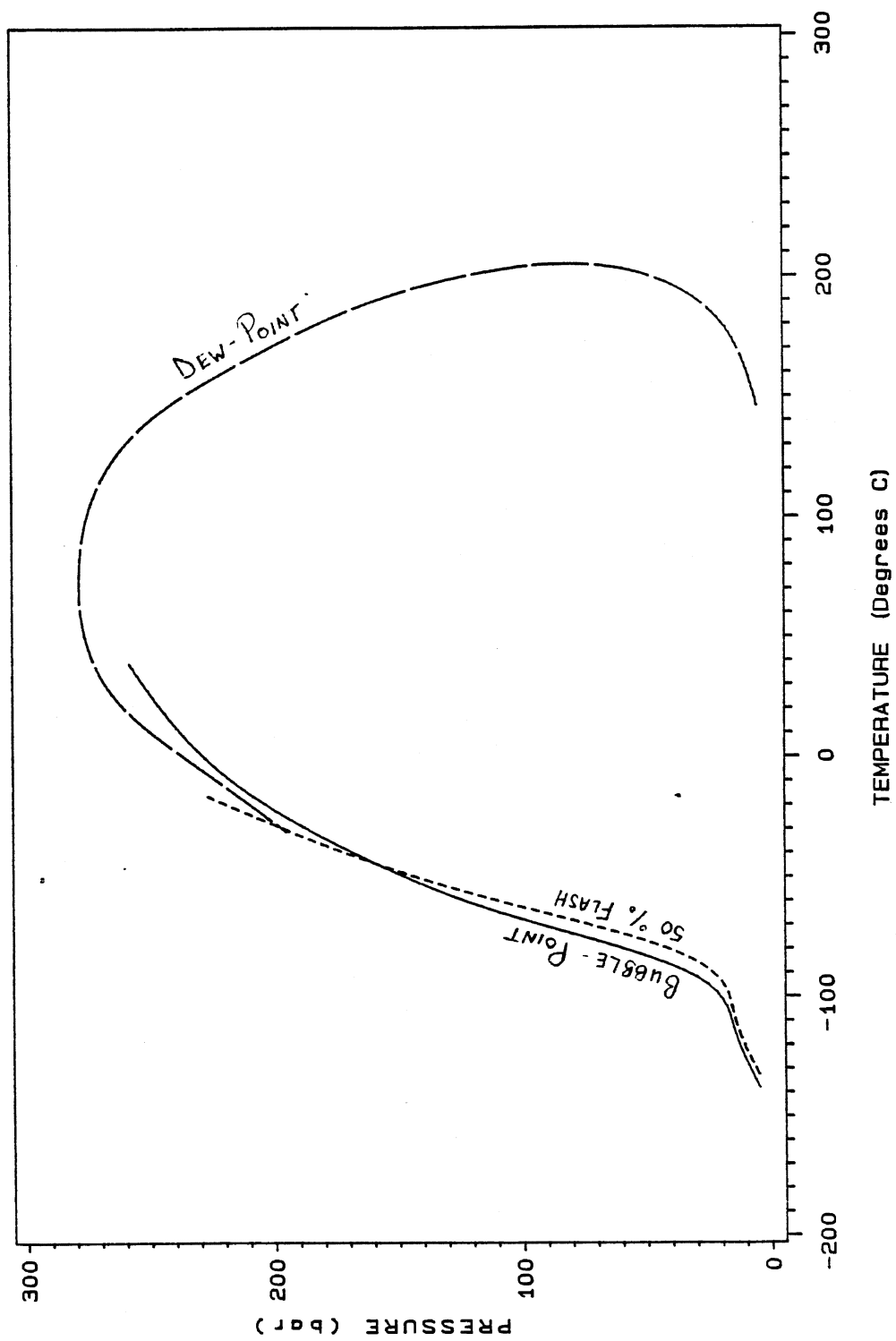
Figure 6. Critical Point Approximation for Mixture 5.

TABLE II

COMPOSITIONS OF MIXTURES

Comp.	Mixture 1	Mixture 2	Mixture 3	Mixture 4	Mixture 5
CO_2	–	–	–	.0987	.0023
N_2	–	–	–	–	.0091
H_2S	–	–	–	.4022	–
C1	.6900	.2019	–	.4988	.3671
C2	–	.2029	.6120	–	.0862
C3	.0750	.2033	–	–	.0846
i-C4	–	–	–	–	.0154
n-C4	.2350	.2038	–	–	.0423
i-C5	–	–	–	–	.0155
n-C5	–	.1881	.2710	–	.0266
n-C7	–	–	.1170	–	–
Frac 1	–	–	–	–	.1225
Frac 2	–	–	–	–	.0931
Frac 3	–	–	–	–	.0648
Frac 4	–	–	–	–	.0444
Frac 5	–	–	–	–	.0261

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.

REFERENCES

Aftab, T., "A Computational Algorithm for Vapor-Liquid
    Equilibria Phase Envelopes." M.S. Thesis, Oklahoma
    State University, Stillwater, 1987.

Baker, L.E. and Luks, K.D., "Critical Point and Saturation
    Pressure Calculations for Multicomponent Systems."
    Soc. Pet. Eng. J., Feb. 1980, 15-24.

Billingsley, D.S. and Lam,S., "Critical Point Calculation
    with Non-Zero Interaction Parameters." AIChE J., vol.
    32, no. 8 (1986), 1393-1396.

Friedemann, J.D., Private communications, Oklahoma State
    University, Stillwater, 1987.

Heidemann, R.A. and Khalil, A.M., "The Calculation of
    Critical Points." AIChE J., vol. 26, no. 5 (1980),
    769-779.

Huron, M., Dufor, G. and Vidal, J., "Vapour-Liquid
    Equilibrium and Critical Locus Curve Calculations with
    the Soave Equation for Hydrocarbon Systems with Carbon
    Dioxide and Hydrogen Sulphide." Fluid Phase Equil. 1
    (1977/78), 247-265.

Li, C.C., "Critical Temperature Estimation for Simple
    Mixtures." Can. J. Chem. Eng., vol. 49 (1971),
    709-710.

Michelsen, M.L. and Heidemann, R.A., "Calculation of
    Critical Points from Cubic Two-Constant Equations of
    State." AIChE J., vol. 27, no. 3 (1981), 521-523.

Michelsen, M.L., "Calculation of Phase Envelopes and
    Critical Points for Multicomponent Mixtures." Fluid
    Phase Equil., 4 (1980), 1-10.

Michelsen, M.L., "The Isothermal Flash Problem. Part 1.
    Stability." Fluid Phase Equil., 9 (1982), 1-19.

Michelsen, M.L., "Calculation of Critical Points and Phase
    Boundaries in the Critical Region." Fluid Phase
    Equil., 16 (1984), 57-76.

Modell, M. and Reid, R.C., "Thermodynamics and its
    Applications", 2nd edition (1983), Prentice-Hall, Inc.

Peng, D. and Robinson, D.B., "A Rigorous Method for
    Predicting the Critical Properties of Multicomponent
    Systems from an Equation of State." AIChE J., vol. 23,
    no. 2 (1977), 137-144.

Reid, R.C. and Beegle, B.L., "Critical Point Criteria in
    Legendre Transform Notation." AIChE J., vol. 23, no. 5
    (1977), 726.

Teja, A.S., Garg, K.B., and Smith, R.L., "A Method for the
    Calculation of Gas-Liquid Critical Temperatures and
    Pressures of Multicomponent Mixtures." Ind. Eng. Chem.
    Process Des. Dev. (1983) 22, 672-676.

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.
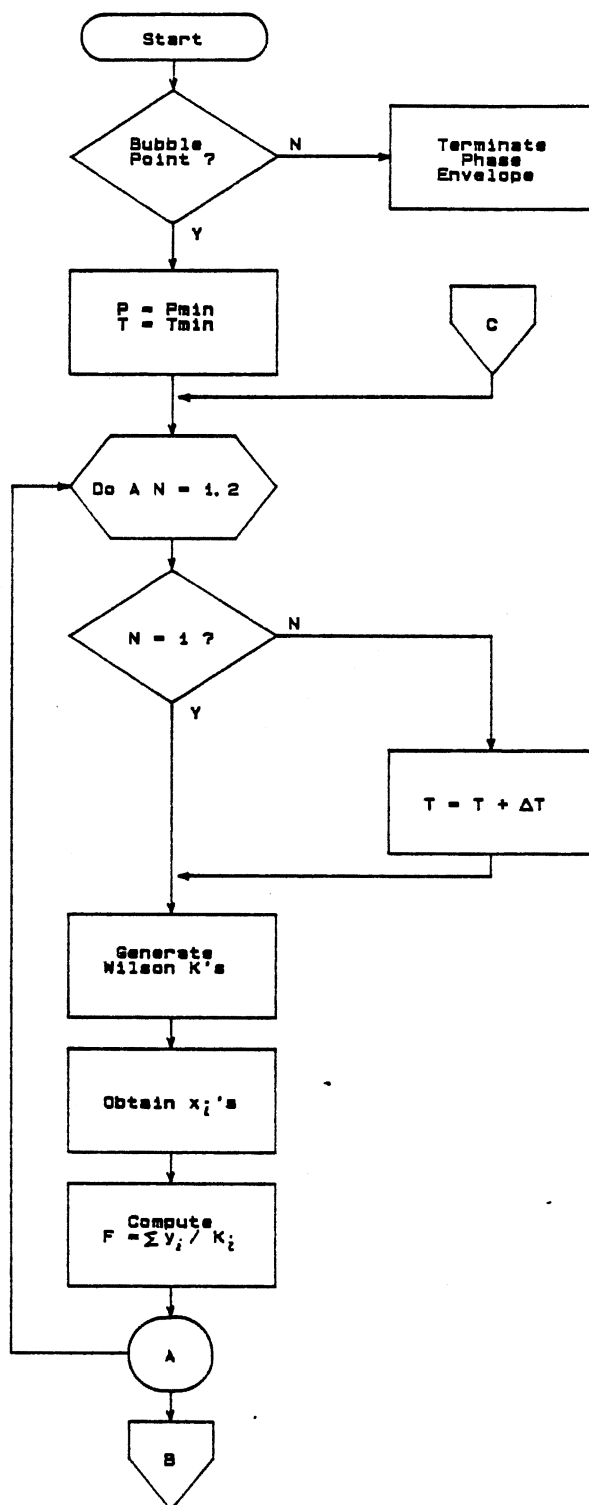
Figure 1.   Initiation of the
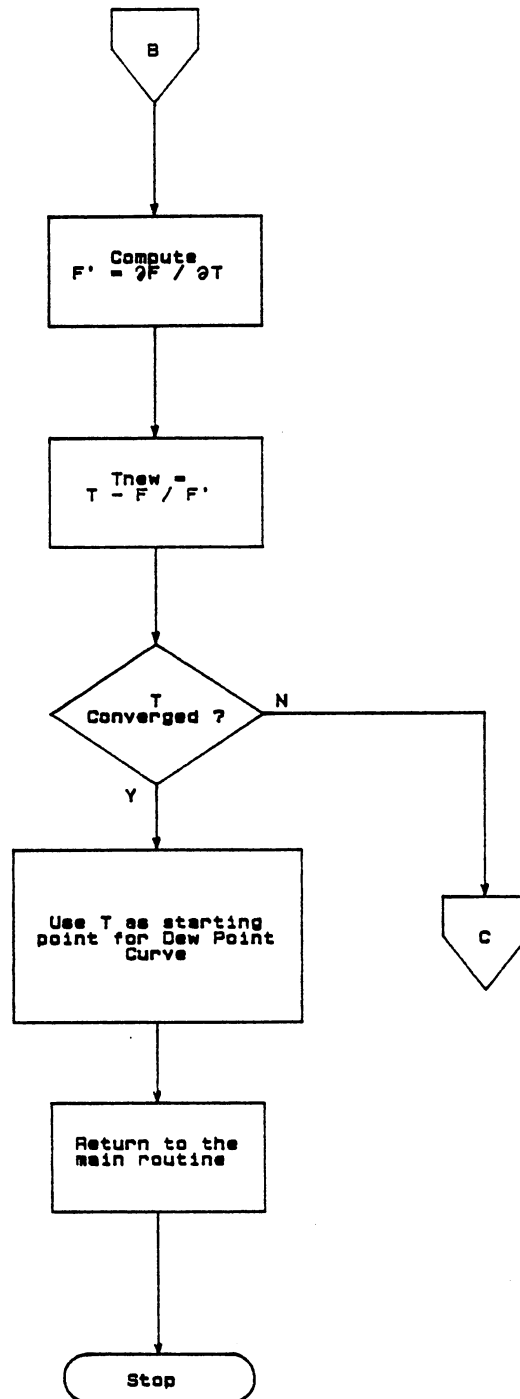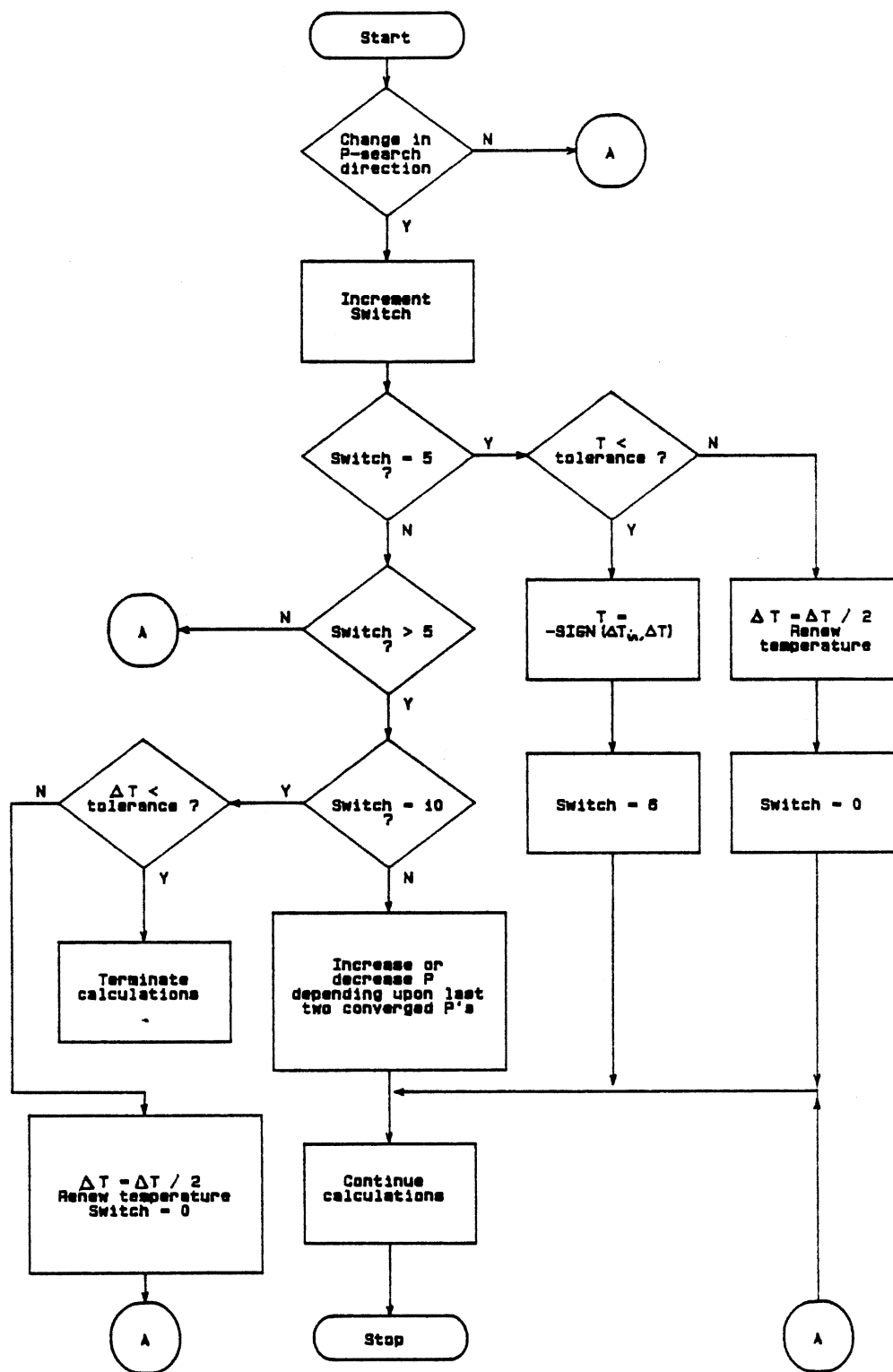   Dew-Point Curve.

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 to 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
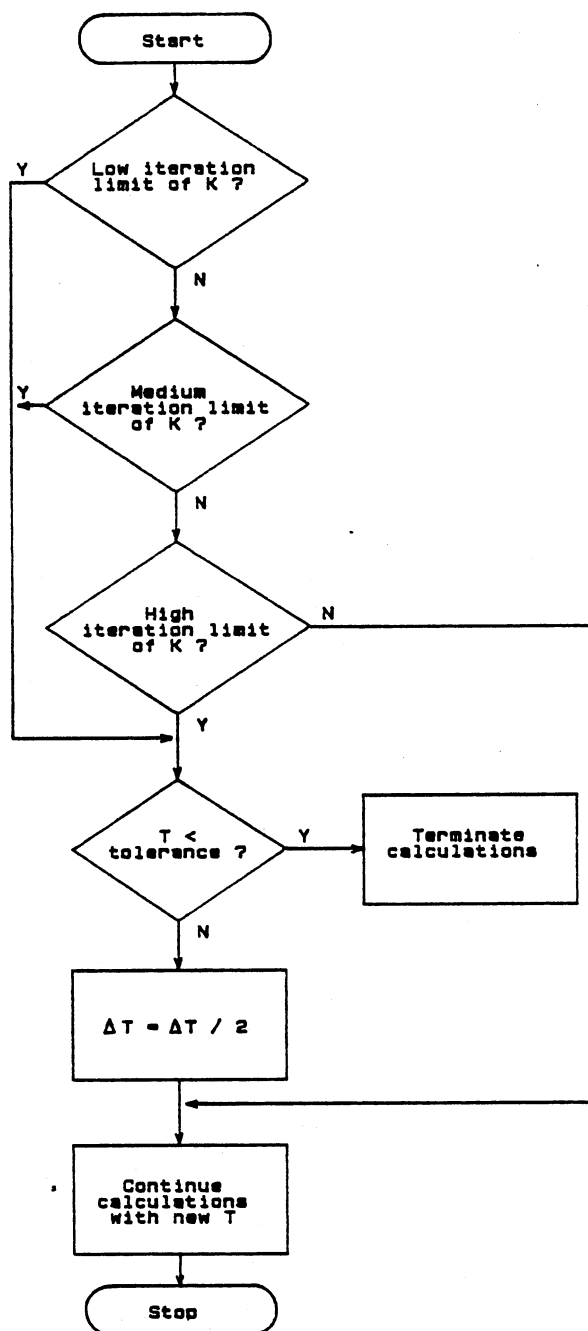
Figure 3. Termination
          Criterion for
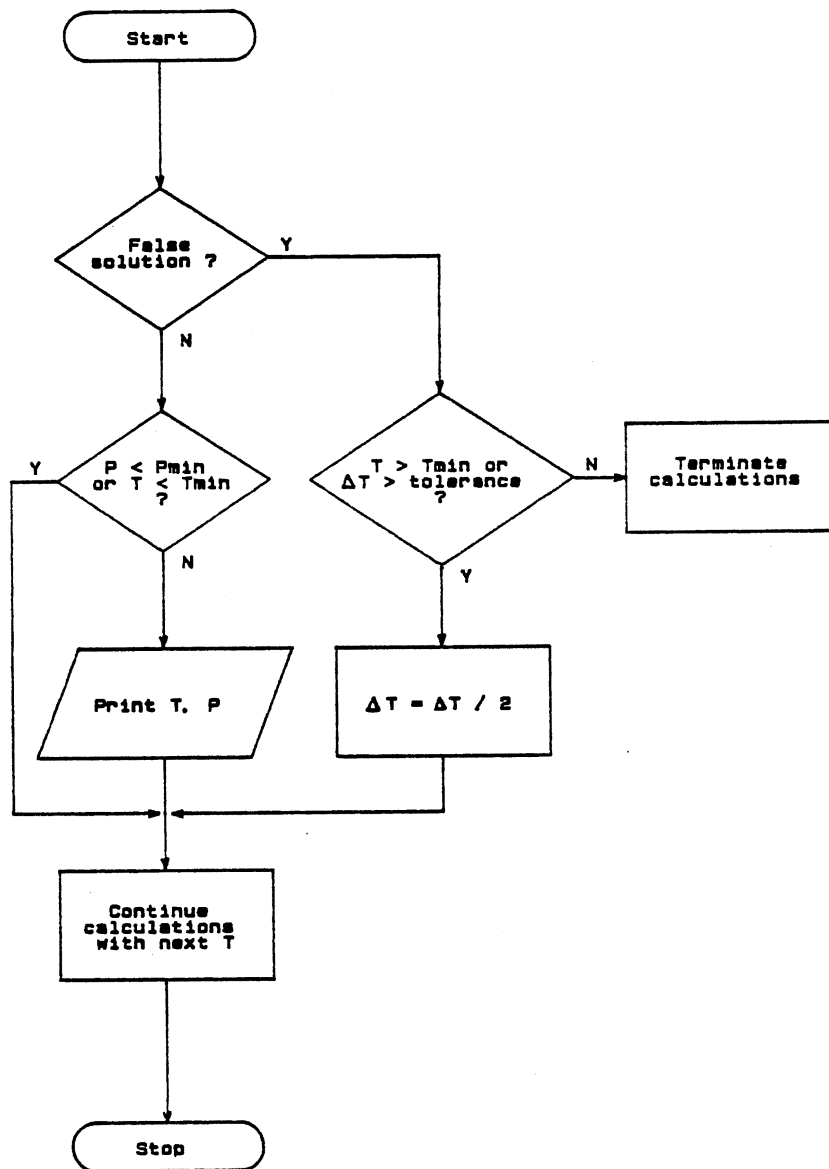   Excessive K-Loop
          Iterations.

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, 's of both liquid and
vapor phases, where ϕ_i is given by:

$$\phi_i^\alpha = \hat{f}_i^\alpha / Px_i^\alpha \tag{1}$$

where   i = i-th component

α = α-phase

$\hat{f}_i$ = component fugacity

P = system pressure

At equilibrium

$$\hat{f}_i^L = \hat{f}_i^V \tag{2}$$

$$P\hat{\phi}_i^V y_i = P\hat{\phi}_i^L x_i \tag{3}$$

$$\Rightarrow \quad y_i/x_i = \hat{\phi}_i^L/\hat{\phi}_i^V = K_i \tag{4}$$

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
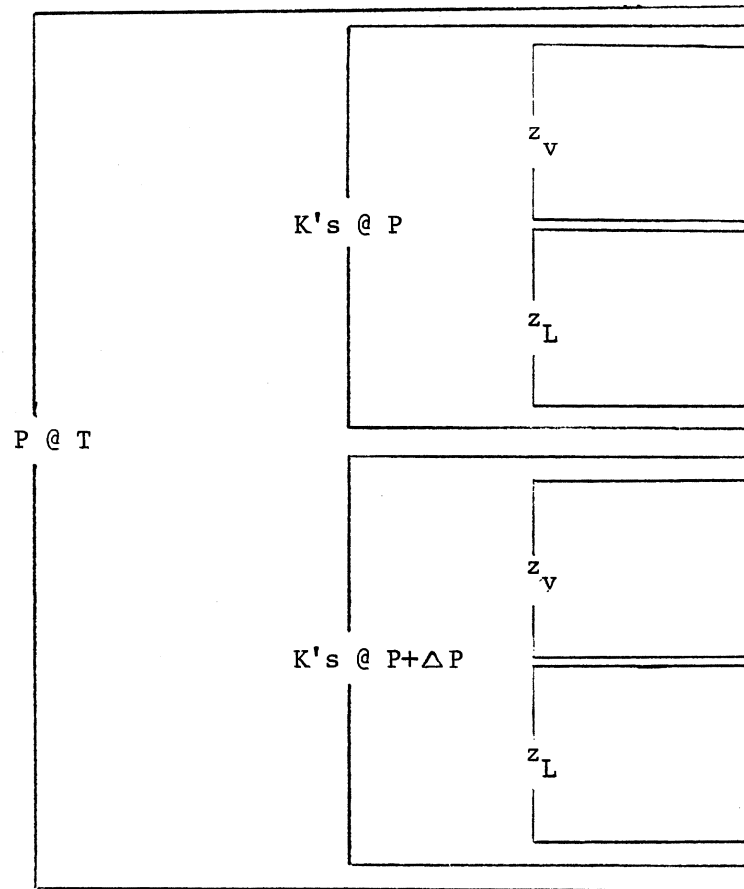
Figure 5. Heirarchy of Nested Loops.

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:

$$g_i = \partial(G/RT)/\partial n_{i_2} = \ln f_{i_2} - \ln f_{i_1} = 0 \qquad (5)$$

$$K_i^{(k+1)} = K_i^{(k)}((f_i^L/f_i^V)^{(k)})^{\gamma^{(k)}} \qquad (6)$$

or,

$$K_i^{(k+1)} = K_i^{(k)}((\phi_i^L/\phi_i^V)^{(k)} 1/K_i^{(k)})^{\gamma^{(k)}} \qquad (7)$$

where,

$$\gamma^{(k)} = \left| \frac{\bar{g}^{(k-1)^T} \bar{g}^{(k-1)}}{\bar{g}^{(k-1)T}(\bar{g}^{(k)} - \bar{g}^{(k-1)})} \right| \qquad (8)$$

and

$$\gamma^{(0)} = \gamma^{(1)} = 1.0 \qquad (9)$$

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.

TABLE I

COMPOSITIONS OF MIXTURES

Comp.	Mixture 1	Mixture 2	Mixture 3	Mixture 4	Mixture 5
N2	–	.0091	.0090	–	.0237
CO2	.1000	.0023	.0080	–	.0031
C1	.8608	.3671	.8200	–	.7319
C2	.0247	.0862	.0640	.4000	.0780
C3	.0067	.0846	.0340	.4000	.0355
i-C4	–	.0154	.0050	–	.0071
n-C4	.0045	.0423	.0120	.2000	.0145
i-C5	–	.0155	.0030	–	.0064
n-C5	.0024	.0266	.0050	–	.0068
n-C6	.0009	–	–	–	.0109
Frac 1	–	.1225	–	–	–
Frac 2	–	.0931	–	–	–
Frac 3	–	.0648	–	–	–
Frac 4	–	.0444	–	–	–
Frac 5	–	.0261	–	–	–
Frac 6	–	–	.0054	–	–
Frac 7	–	–	.0050	–	–
Frac 8	–	–	.0047	–	–
Frac 9	–	–	.0045	–	–
Frac 10	–	–	.0042	–	–
Frac 11	–	–	.0039	–	–
Frac 12	–	–	.0035	–	–
Frac 13	–	–	.0032	–	–
Frac 14	–	–	.0029	–	–
Frac 15	–	–	.0026	–	–
Frac 16	–	–	–	–	.0325
Frac 17	–	–	–	–	.0214
Frac 18	–	–	–	–	.0114
Frac 19	–	–	–	–	.0098
Frac 20	–	–	–	–	.0071

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.
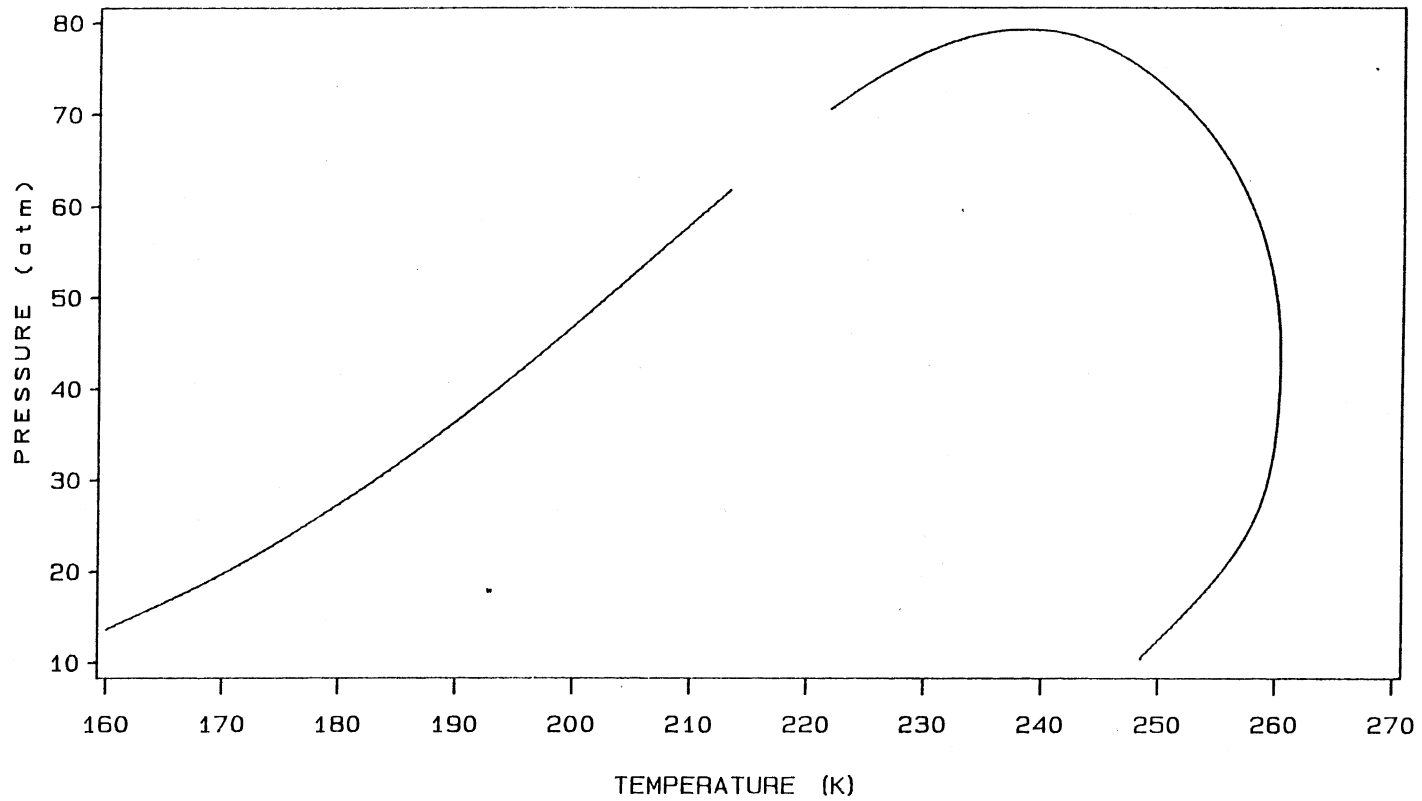
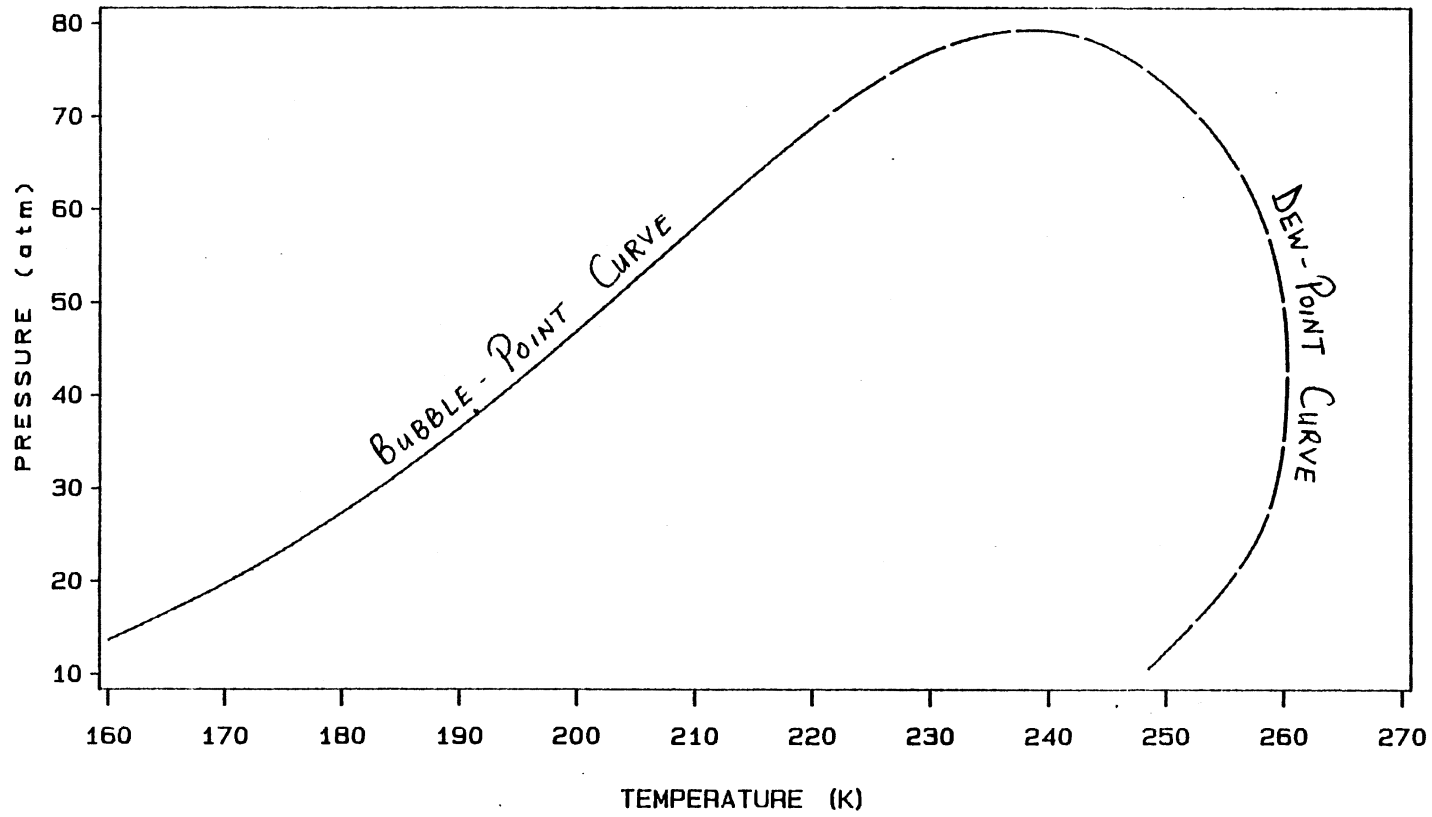Figure 6. Phase Envelope of Mixture 1
At a Tolerance of 0.2 K.

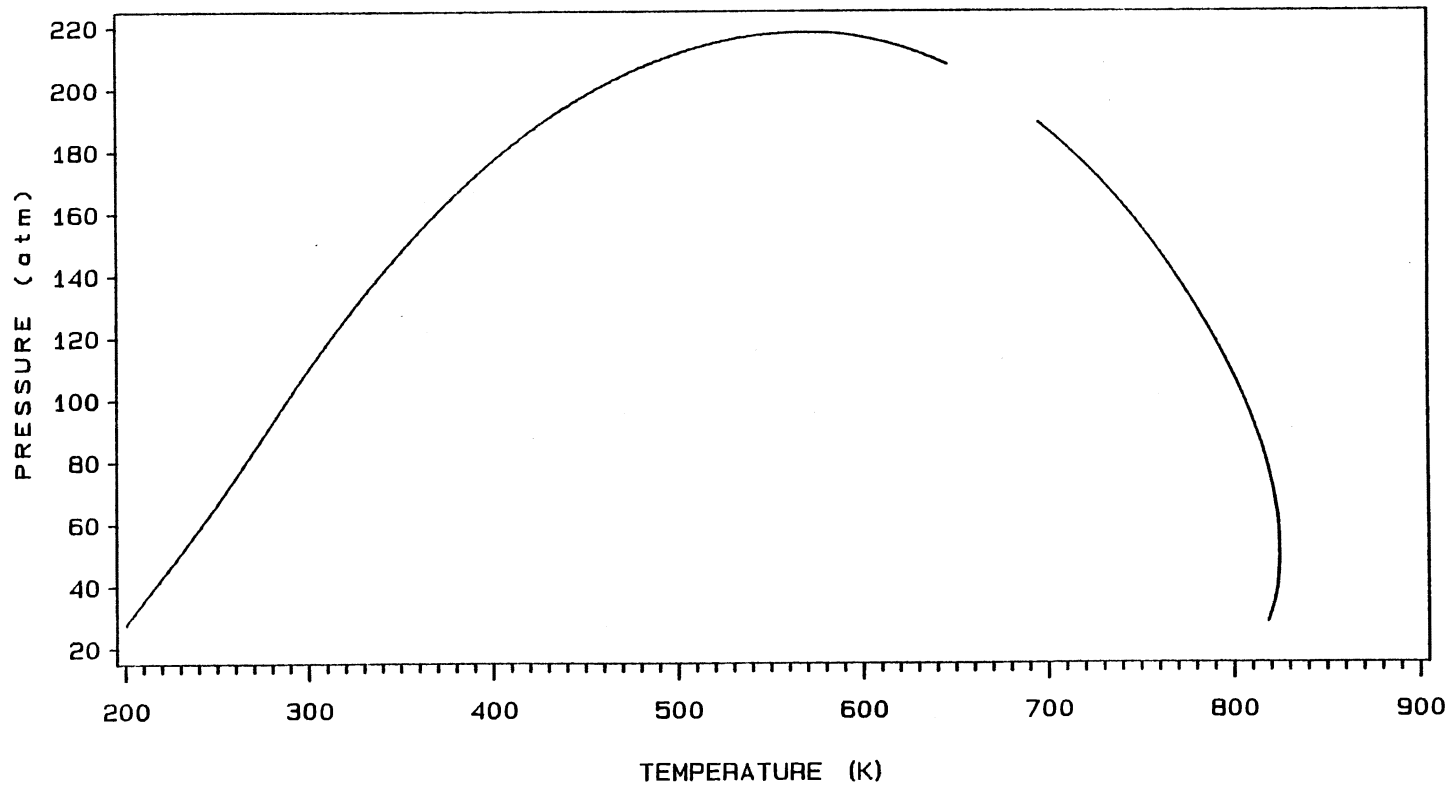Figure 7. Phase Envelope of Mixture 1
At a Tolerance of 0.1 K.

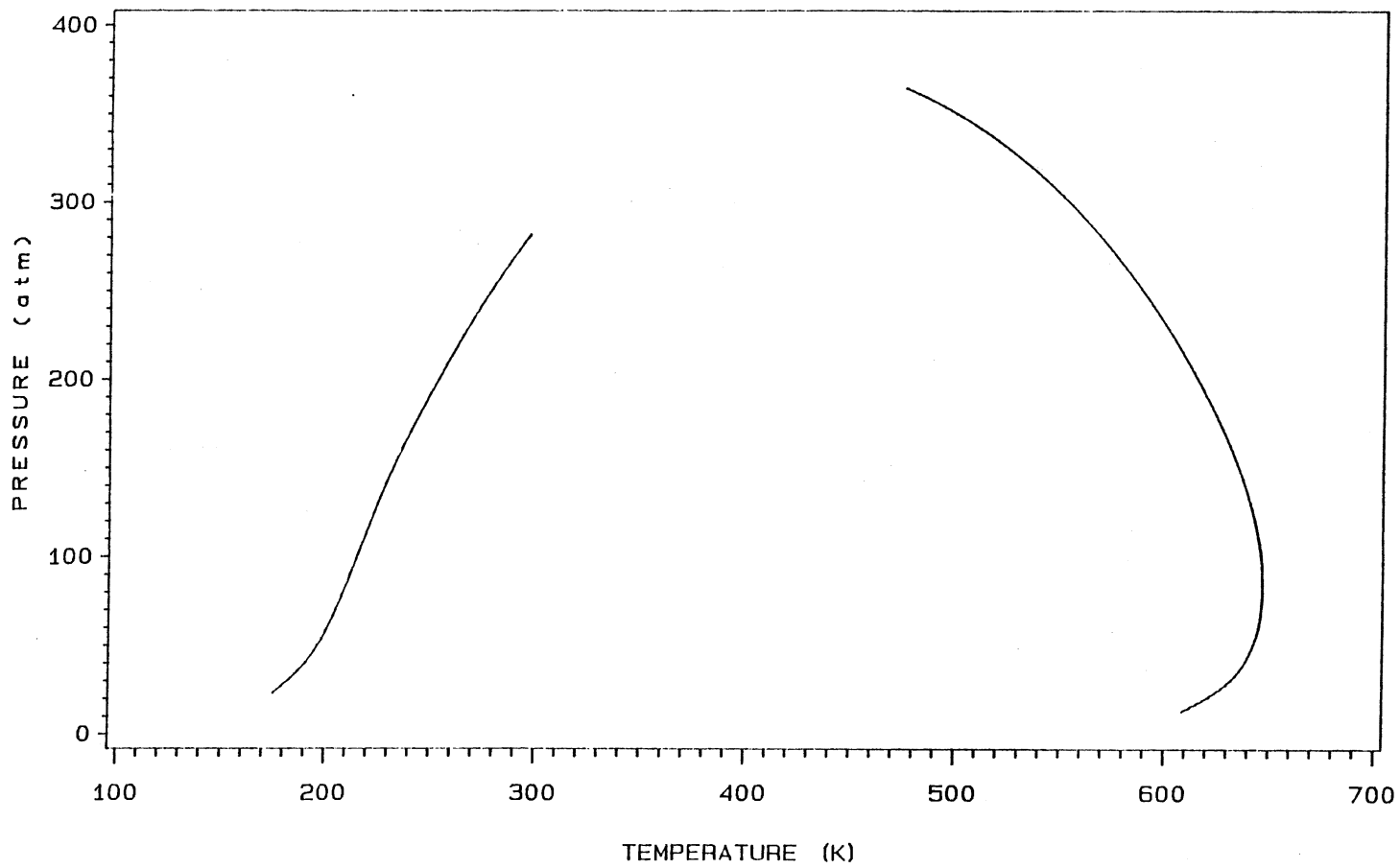Figure 8.   Phase Envelope of Mixture 2.
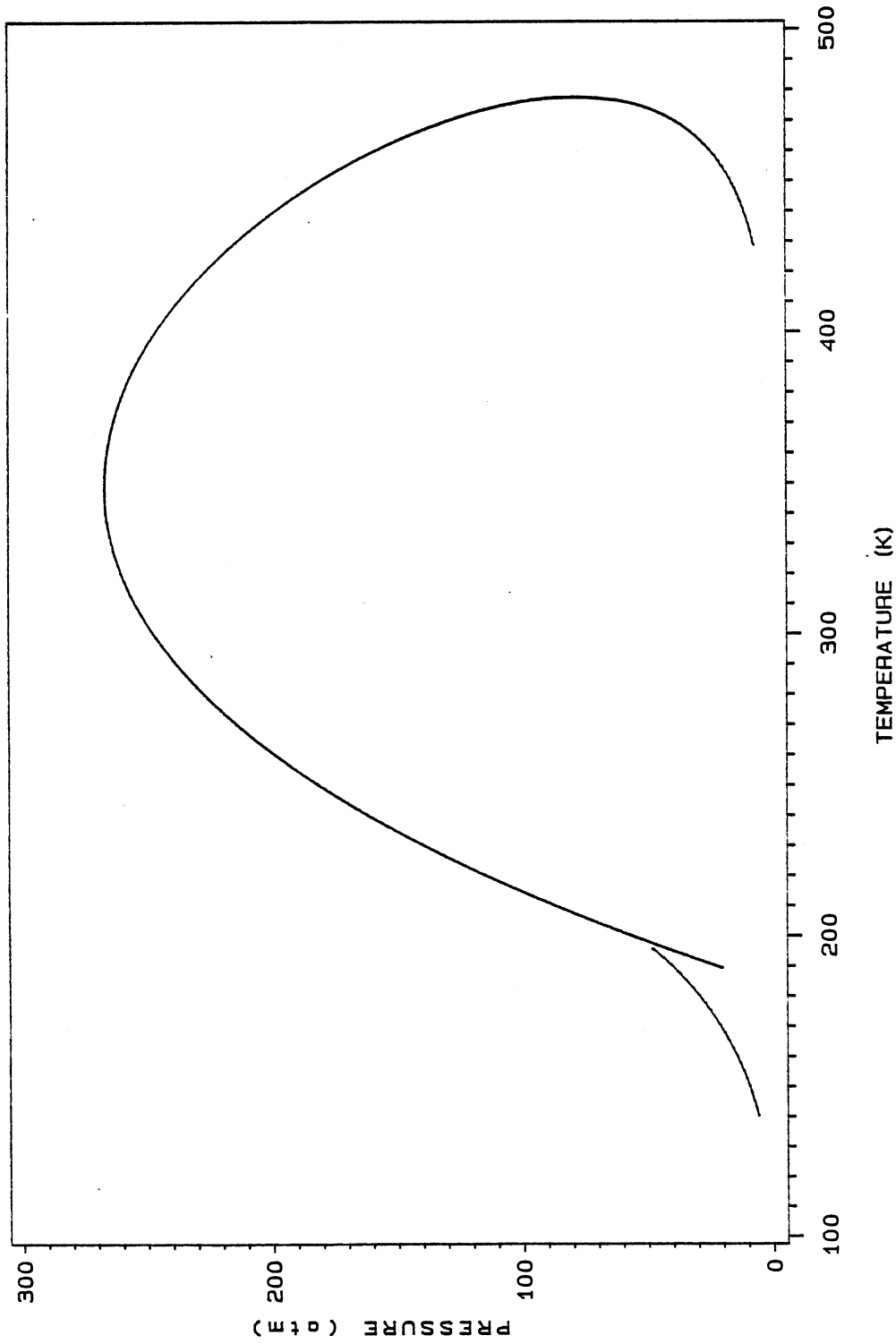
Figure 9. Phase Envelope of Mixture 5.
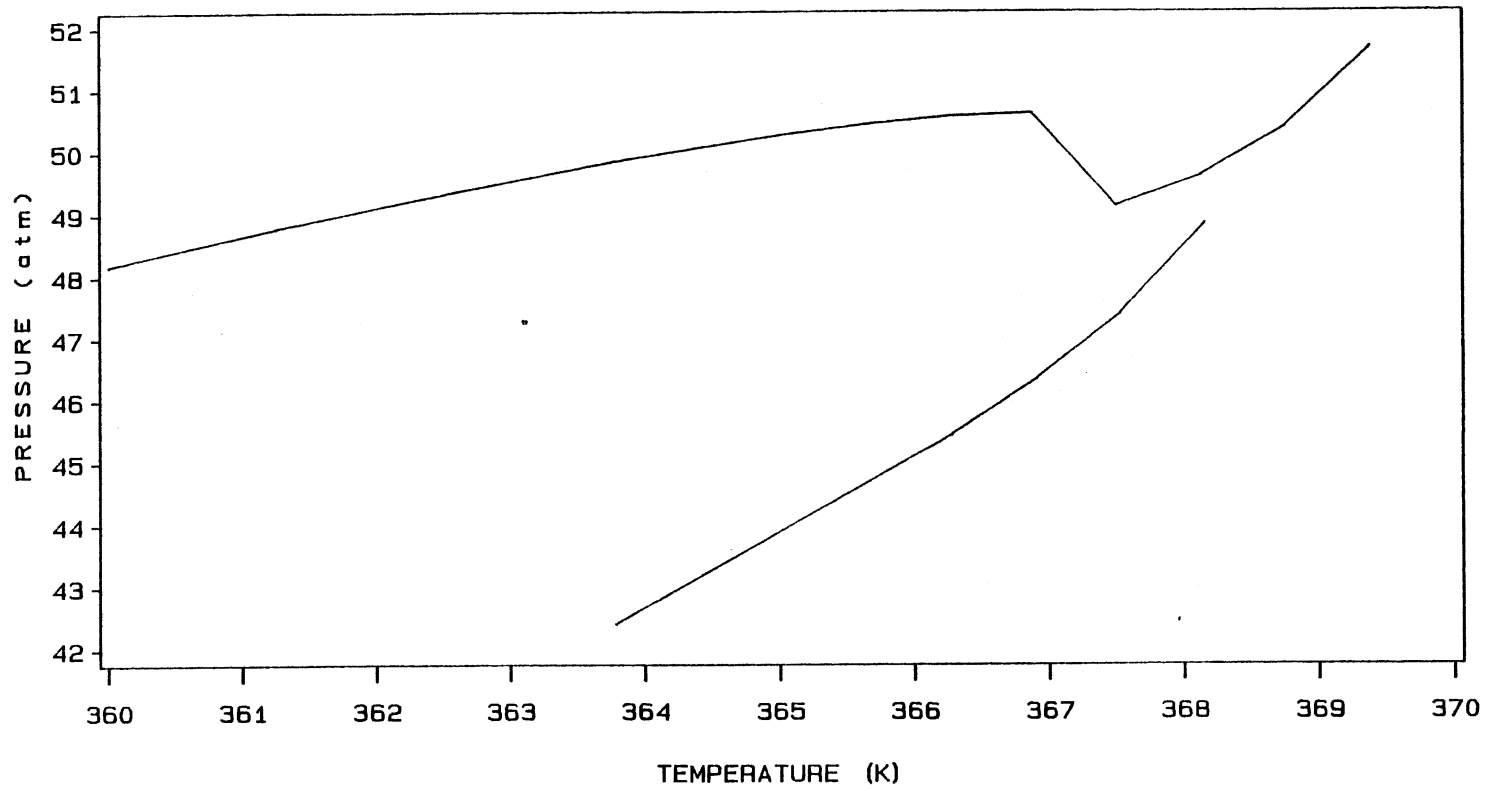
Figure 10. Phase Envelope of Mixture 3.

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

System	CPU Time w/ accelerator (m:s)	CPU Time w/o accelerator (m:s)
Mixture 1	10:47.04	12:32.93
Mixture 2	18:44.86	25:30.69
Mixture 3	05:59.88	09:23.22
Mixture 4	00:12.49	00:13.13
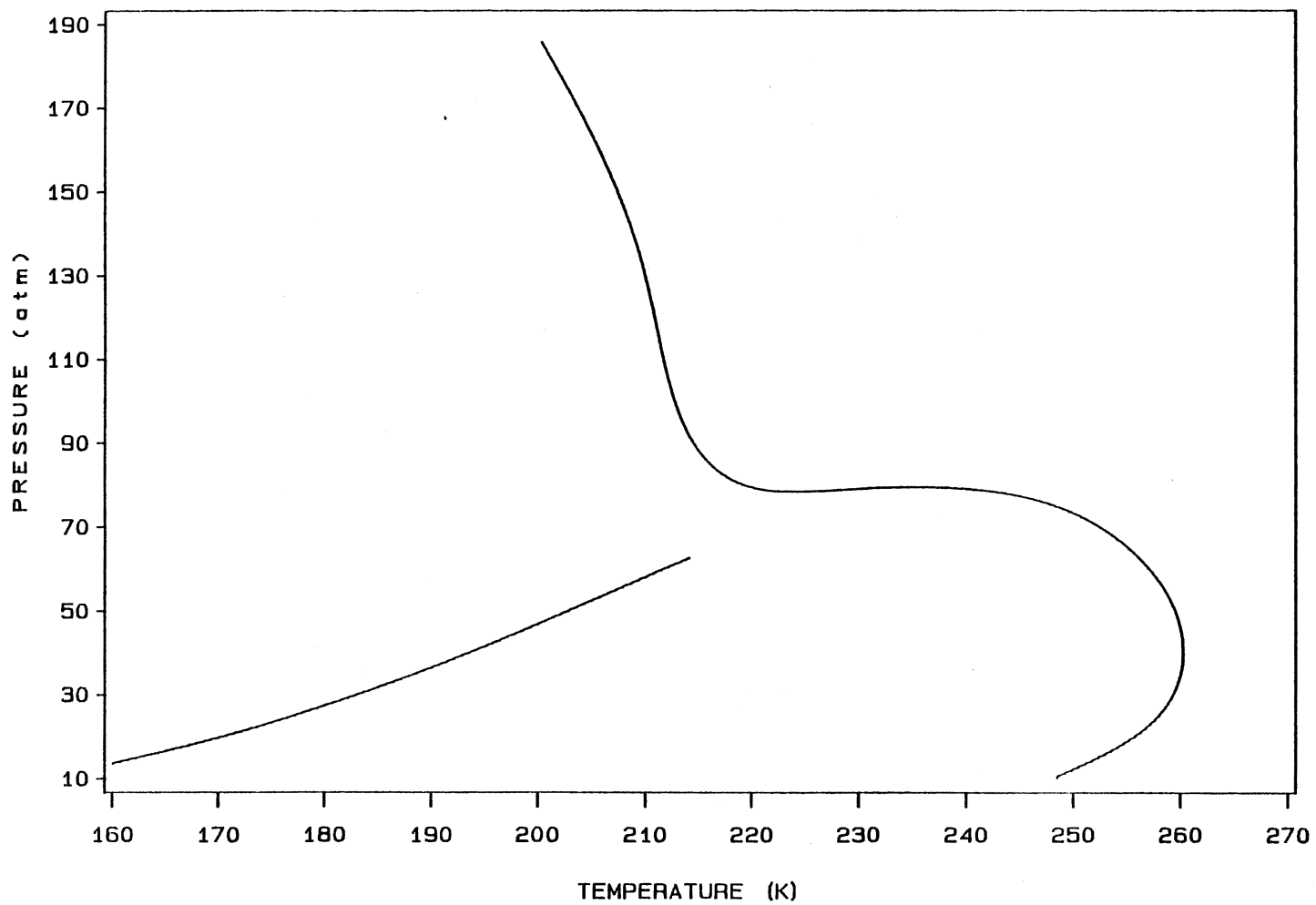
Figure 12. Failure of Acceleration (Mixture 1).

TABLE III

PHASE ENVELOPE CALCULATIONS

Temp.(K)	Press.(atm)	P-loop Itr.	K-loop Itr.
		BUBBLE-POINT CURVE	
160.00	13.72	8	3
170.00	19.80	4	3
180.00	27.40	4	4
190.00	36.51	4	5
200.00	46.95	4	7
205.00	52.53	4	23
210.00	58.17	4	23
212.50	60.96	4	46
213.75	62.34	4	74
215.00	63.69	4	129
215.63	64.37	4	194
		DEW-POINT CURVE	
248.51	10.64	4	2
258.51	26.79	5	5
259.14	29.29	3	13
259.76	32.81	4	5
260.07	35.58	4	11
260.23	38.00	4	8
250.23	73.11	5	12
240.23	79.18	4	20
235.23	78.93	2	31
230.23	76.99	7	55
225.23	73.59	9	90
222.73	71.46	9	146
221.48	70.30	7	195

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.

REFERENCES

Aftab, T., "A Computational Algorithm for Vapor-Liquid Equilibria Phase Envelopes." M.S. Thesis, Oklahoma State University, Stillwater, 1987.

Boston, J.F. and Britt, H.I., "A Radically Different Formulation and Solution of the Single-Stage Flash Problem." Comp. and Chem. Eng., vol. 2 (1978), 109-122.

Fussell, D.D. and Yanosik, J.L., "An Iterative Sequence for Phase-Equilibria Calculations Incorporating the Redlich-Kwong Equation of State." Soc. of Pet. Eng. J., June, 1978, 173-182.

Heidemann, R.A., "Computation of High Pressure Phase Equilibria." Fluid Phase Equil., 14 (1983), 55-78.

Mehra, R.K., Heidemann, R.A. and Aziz, K., "Computation of Multiphase Equilibria for Compositional Simulation." Soc. of Pet. Eng. J., Feb. 1982, 61-68.

Mehra, R.K., Heidemann, R.A. and Aziz, K., "An Accelerated Successive Substitution Algorithm." Can. J. Chem. Eng., vol. 61, Aug. 1983, 590-596.

Michelsen, M.L., "Calculation of Phase Envelopes and Critical Points for Multicomponent Mixtures." Fluid Phase Equil., 4 (1980), 1-10.

Michelsen, M.L., "The Isothermal Flash Problem. Part II. Phase-Split Calculation." Fluid Phase Equil. 9 (1982), 21-40.

Michelsen, M.L., "Saturation Point Calculations." Fluid Phase Equil., 23 (1985), 181-192.

Nghiem, L.X., Aziz, K. and Li, Y.K., "A Robust Iterative Method for Flash Calculations Using the Soave-Redlich-Kwong or the Peng-Robinson Equation of State." Soc. of Pet. Eng. J., June, 1983, 521-530.

Nghiem, L.X. and Heidemann, R.A., "General Acceleration
    Procedure for Multiphase Flash Calculation with
    Application to Oil-Gas-Water Systems." Paper presented
    at the 2nd European Symposium on Enhanced Oil Recovery,
    Paris, 1982.

Rijkers, M.P.W. and Heidemann, R.A., "Convergence Behavior
    of Single Stage Flash Calculations." Amer. Chem. Soc.
    Symposium on "Equations of State - Theory and
    Applications", Miami Beach, Florida, April 28 - May 3,
    1985.

Robinson, D.B., Peng, D. and Ng, N., "Capability of the
    Peng-Robinson Programs. Part 1 - VLE and Critical
    Property Calculations." Hydrocarbon Processing, April
    1978, 95-98.

Westman, K.R., Lucia, A. and Miller, D.C., "Flash and
    Distillation Calculations by a Newton-Like Method."
    Comp. and Chem. Eng., vol. 8, nos. 3/4 (1984), 219-228.

Whitson, C.H. and Torp, S.B., "Evaluating Constant-Volume
    Depletion Data." J. of Pet. Technology, March 1983,
    610-620.

BIBLIOGRAPHY

Anderson, T.F. and Prausnitz, J.M., "Computational Methods
    for High-Pressure Phase Equilibria and Other
    Fluid-Phase Properties Using a Partition Function. 2.
    Mixtures." Ind. Eng. Chem. Process Des. Dev., 19
    (1980), 9-14.

Asselineau, L., Bogdanic, G. and Vidal, J., "A Versatile
    Algorithm for Calculating Vapor-Liquid Equilibria."
    Fluid Phase Equil., 3 (1979), 273-290.

Beyer, W.H. (editor), "Standard Mathematical Tables", 27th
    edition, 1984. The CRC Press: 9-11.

Billingsley, D.S. and Lam,S., "Critical Point Calculation
    with Non-Zero Interaction Parameters." AIChE J., vol.
    32, no. 8 (1986), 1393-1396.

Boston, J.F. and Britt, H.I., "A Radically Different
    Formulation and Solution of the Single-Stage Flash
    Problem." Comp. and Chem. Eng., vol. 2 (1978),
    109-122.

Friedemann, J.D., Private communications, Oklahoma State
    University, Stillwater, 1987.

Fussell, D.D. and Yanosik, J.L., "An Iterative Sequence for
    Phase-Equilibria Calculations Incorporating the
    Redlich-Kwong Equation of State." Soc. of Pet. Eng.
    J., June, 1978, 173-182.

Gosset, R., Heyen, G. and Kalitventzeff, B., "An Efficient
    Algorithm to Solve Cubic Equations of State." Fluid
    Phase Equil., 25 (1986), 51-64.

Gundersen, T., "Numerical Aspects of the Implementation of
    Cubic Equations of State in Flash Calculation
    Routines." Comp. and Chem. Eng., vol. 6, no. 3
    (1982), 245-255.

Hankinson, R.W. and Thomson, G.H., "Calculating Liquid
    Densities Accurately." Hydrocarbon Processing, Sept.
    1979, 277-283.

Heidemann, R.A., "Computation of High Pressure Phase
    Equilibria." Fluid Phase Equil., 14 (1983), 55-78.

Heidemann, R.A. and Khalil, A.M., "The Calculation of
    Critical Points." AIChE J., vol. 26, no. 5 (1980),
    769-779.

Huron, M., Dufor, G. and Vidal, J., "Vapour-Liquid
    Equilibrium and Critical Locus Curve Calculations with
    the Soave Equation for Hydrocarbon Systems with Carbon
    Dioxide and Hydrogen Sulphide." Fluid Phase Equil. 1
    (1977/78), 247-265.

Jovanovic, S. and Paunovic, R., "Generating Appropriate
    Density Values From Cubic State Equations to Avoid
    False Unit K Values. Application to Distillation
    Problems." Ind. Eng. Chem. Process Des. Dev. (1984)
    23, 801-805.

Li, C.C., "Critical Temperature Estimation for Simple
    Mixtures." Can. J. Chem. Eng., vol. 49 (1971),
    709-710.

Mehra, R.K., Heidemann, R.A. and Aziz, K., "Computation of
    Multiphase Equilibria for Compositional Simulation."
    Soc. of Pet. Eng. J., Feb. 1982, 61-68.

Mehra, R.K., Heidemann, R.A. and Aziz, K., "An Accelerated
    Successive Substitution Algorithm." Can. J. Chem. Eng.,
    vol. 61, Aug. 1983, 590-596.

Michelsen, M.L., "Calculation of Phase Envelopes and
    Critical Points for Multicomponent Mixtures." Fluid
    Phase Equil., 4 (1980), 1-10.

Michelsen, M.L., "The Isothermal Flash Problem. Part 1.
    Stability." Fluid Phase Equil., 9 (1982), 1-19.

Michelsen, M.L., "The Isothermal Flash Problem. Part II.
    Phase-Split Calculation." Fluid Phase Equil. 9 (1982),
    21-40.

Michelsen, M.L., "Calculation of Critical Points and Phase
    Boundaries in the Critical Region." Fluid Phase
    Equil., 16 (1984), 57-76.

Michelsen, M.L., "Saturation Point Calculations." Fluid
    Phase Equil., 23 (1985), 181-192.

Michelsen, M.L. and Heidemann, R.A., "Calculation of
    Critical Points from Cubic Two-Constant Equations of
    State." AIChE J., vol. 27, no. 3 (1981), 521-523.

Modell, M. and Reid, R.C., "Thermodynamics and its Applications", 2nd edition (1983), Prentice-Hall, Inc.

Nghiem, L.X., Aziz, K. and Li, Y.K., "A Robust Iterative Method for Flash Calculations Using the Soave-Redlich-Kwong or the Peng-Robinson Equation of State." Soc. of Pet. Eng. J., June, 1983, 521-530.

Nghiem, L.X. and Heidemann, R.A., "General Acceleration Procedure for Multiphase Flash Calculation with Application to Oil-Gas-Water Systems." Paper presented at the 2nd European Symposium on Enhanced Oil Recovery, Paris, 1982.

Peng, D. and Robinson, D.B., "A Rigorous Method for Predicting the Critical Properties of Multicomponent Systems from an Equation of State." AIChE J., vol. 23, no. 2 (1977), 137-144.

Poling, B.E., Grens II, E.A. and Prausnitz, J.M., "Thermodynamic Properties from a Cubic Equation of State: Avoiding Trivial Roots and Spurious Derivatives." Ind. Eng. Chem. Process Des. Dev., 20 (1981), 127-130.

Rackett, H.G., "Equation of State for Saturated Liquids." J. of Chem. and Eng. Data, vol. 15, no. 4 (1970), 514-517.

Reid, R.C. and Beegle, B.L., "Critical Point Criteria in Legendre Transform Notation." AIChE J., vol. 23, no. 5 (1977), 726.

Reid, R.C., Prausnitz, J.M. and Sherwood, T.K., "The Properties of Gases and Liquids", 3rd edition (1977), McGraw-Hill Book Company.

Rijkers, M.P.W. and Heidemann, R.A., "Convergence Behavior of Single Stage Flash Calculations." Amer. Chem. Soc. Symposium on "Equations of State - Theory and Applications", Miami Beach, Florida, April 28 - May 3, 1985.

Robinson, D.B., Peng, D. and Ng, N., "Capability of the Peng-Robinson Programs. Part 1 - VLE and Critical Property Calculations." Hydrocarbon Processing, April 1978, 95-98.

Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State." Chem. Eng. Sci., 27 (1972), 1197-1203.

Teja, A.S., Garg, K.B., and Smith, R.L., "A Method for the Calculation of Gas-Liquid Critical Temperatures and Pressures of Multicomponent Mixtures." Ind. Eng. Chem. Process Des. Dev. (1983) 22, 672-676.

Thomson, G.H., Brobst, K.R. and Hankinson, R.W., "An Improved Correlation for Densities of Compressed Liquids and Liquid Mixtures." AIChE J., vol. 28, no. 4 (1982), 671-676.

Veerana, D. and Rihani, D.N., "Avoiding Convergence Problems in VLE Predictions Using an Equation of State." Fluid Phase Equil., 16 (1984), 41-55.

Westman, K.R., Lucia, A. and Miller, D.C., "Flash and Distillation Calculations by a Newton-Like Method." Comp. and Chem. Eng., vol. 8, nos. 3/4 (1984), 219-228.

Whitson, C.H. and Torp, S.B., "Evaluating Constant-Volume Depletion Data." J. of Pet. Technology, March 1983, 610-620.

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