Formulations for Three-Phase Flash Calculations

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A study of flash equations associated with multicomponent systems that can form three phases at a given temperature and pressure indicated that different equations are needed at different boundaries of the solution space. This problem dictates that one- and two-phase trial solutions be obtained first on the boundaries prior to a search in the three-phase interior region. Two new formulations of the flash equations have been developed to avoid this problem. Solutions at boundaries as well as those in the three-phase region can now be obtained with a single search procedure. The new formulations are made using functions that are monotonic in the selected coordinates. These properties facilitate the use of nested, single-variable search methods. Interpolating with second-order functions, when applicable, nested search methods are often faster than two-dimensional simultaneous search methods. Tests of these formulations have demonstrated the advantages of these characteristics.

Introduction

In a sequential modular process simulation system, such as FLOWTRAN or ASPEN, unit-operations modules must produce results reliably and efficiently for different physical-property models and over broad operating ranges. In general, speed and reliability of obtaining iterative solutions depend on the algorithm used. However, these convergence properties are also affected by model formulation.

For example, in a vapor-liquid two-phase flash calculation, likely the most frequently used module in a simulator, the commonly accepted formulation of the equilibrium condition has been critical to obtaining solutions rapidly and reliably. This novel formulation was attributed to Rachford and Rice (1952). Instead of searching for the root of $\Sigma y_i = 1$ or $\Sigma x_i = 1$, they recommended $\Sigma(x-y)_i = 0$. This slight change in formulation eliminates numerical problems associated with multiple roots. The monotonic property of their formulation improves the speed of convergence and avoids the need to test for single-phase solutions.

It is commonly recognized that three-phase flash calculations are more difficult than those with only two phases. The reliability of these calculations depends very much on initial estimates of composition. However, some problems are caused by the formulation used. In this work, we identified the specific problems with the commonly accepted formulation, developed two improved formulations, and showed their desirable characteristics in three-phase flash calculations. The speed and reliability improvements in convergence were realized with their use over the last five years at Monsanto.

Problems with the Current Formulation

Three-phase flash equations

Equations applicable to the three-phase flash system are:

Material balances:

$$Fz_i = Vy_i + L_1x_{1i} + L_2x_{2i}; \quad i = 1, \ldots, n \tag{1}$$

Phase relations:

$$y_i = K_{1i}x_{1i}; \quad i = 1, \ldots, n \tag{2}$$

$$y_i = K_{2i}x_{2i}; \quad i = 1, \ldots, n \tag{3}$$

Equilibrium conditions:

$$S_v \equiv \Sigma y_i = 1, \quad \text{if the vapor phase exists.} \tag{4}$$

$$S_1 \equiv \Sigma x_{1i} = 1, \quad \text{if the liquid phase 1 exists.} \tag{5}$$

$$S_2 \equiv \Sigma x_{2i} = 1, \quad \text{if the liquid phase 2 exists.} \tag{6}$$

Variables are defined in the notation section. When used in conjunction with the specific algorithm described later, variables z, F, and K are given and $S_f \equiv \Sigma z_i$ is 1. The above $3n+3$ equations are solved numerically to obtain values for V, L_1, L_2, y, x_1, and x_2.

The first three equations are usually combined into equations for y_i:

$$y_i = \frac{z_i}{(1-R_1-R_2)+\frac{R_1}{K_{1i}}+\frac{R_2}{K_{2i}}}; \quad i=1, \ldots, n \tag{7}$$

where:

$$R_1 \equiv \frac{L_1}{F}$$

$$R_2 \equiv \frac{L_2}{F}$$

In the following, we also use the variable R_v defined as:

$$R_v \equiv \frac{V}{F} = 1 - R_1 - R_2$$

Two-phase formulation

In typical two-phase ($R_2 = 0$) algorithms (Boston and Britt, 1978; Chien, 1984) for flash calculations with specified outlet temperature and pressure, the K-values are calculated with estimated compositions first. The algorithm then searches for a value of R_1 such that y calculated from Eq. 7 satisfy Eq. 4 or 5. The resulting compositions are then used in generating improved estimates of compositions until the composition-iterative loop is converged.

As shown by Rachford and Rice (1952), Eq. 4 is not monotonic with R_1 and has two roots, one of which is trivial at $R_1 = 0$. Equation 5 behaves similarly. Their solution to this problem was very simple. Instead of Eq. 4 or 5, they used the difference:

$$Q_{1v} \equiv \Sigma x_{1i} - \Sigma y_i = 0 \tag{8}$$

This formulation is monotonic and hence eliminates the trivial root. The partial derivative of this difference with respect to R_1 is:

$$\frac{\partial(\Sigma x_{1i} - \Sigma y_i)}{\partial R_1} = -\sum \frac{(x_{1i}-y_i)^2}{z_i} \tag{9}$$

Since the righthand side is always negative, the difference is monotonic-decreasing with respect to R_1 and can have only one root (or none at all). In the example described later for a three-phase problem, the behavior of the difference function is shown graphically.

There is another important property of this formulation resulting from its being monotonic. When the solution is outside the range between the bubble and dew points (that is, Eqs. 4 and 5 are not satisfied simultaneously), a search method designed to find the least deviation from zero of this difference can locate the correct value for R_1 at one of the bounds. With this property, the same formulation can be used for finding a solution at the single-phase boundaries as well as in the two-phase region. Not having to switch governing equations in the search is an important contributing factor to the speed of solution algorithms. An application of this idea to adiabatic flash calculations was given by Chien (1984).

Three-phase formulation in use

Algorithms for three-phase flash calculations with specified outlet temperature and pressure (Henley and Rosen, 1969; Nelson, 1987) are very similar to those for two-phase algorithms. There is on the outside the composition convergence (or outer) loop. Inside the composition loop, flow ratios must be found in the inner loop to satisfy Eqs. 4, 5, and 6. Recognizing the success of Rachford and Rice, most investigators avoided the direct application of Eqs. 4, 5, and 6 but instead used Eq. 8 and the following difference:

$$Q_{2v} \equiv \Sigma x_{2i} - \Sigma y_i = 0 \tag{10}$$

This difference is monotonic with respect to R_2:

$$\frac{\partial(\Sigma x_{2i} - \Sigma y_i)}{\partial R_2} = -\sum \frac{(x_{2i}-y_i)^2}{z_i} \tag{11}$$

The algorithm for the inner loop searches for R_1 and R_2 in the two-dimensional (R_1, R_2) space bounded by $R_1 = 0$, $R_2 = 0$, and $R_1 + R_2 = 1$ such that y, x_1, and x_2 calculated from Eqs. 7, 2, and 3 satisfy Eqs. 8 and 10.

Equations 8 and 10 exhibit acceptable characteristics in the three-phase region. However, on the line $R_1 + R_2 = 1$, these equations are not usable since S_v may be less than 1 at the solution. For these cases (liquid/liquid equilibria), most investigators defined the following difference:

$$Q_{21} \equiv \Sigma x_{2i} - \Sigma x_{1i} = 0. \tag{12}$$

Equation 7 can be rewritten in terms of R_v and R_L.

$$y_i = \frac{z_i}{R_v + \frac{(1-R_v)R_L}{K_{1i}} + \frac{(1-R_v)(1-R_L)}{K_{2i}}}; \quad i=1, \ldots, n \tag{13}$$

where:

$$R_L \equiv \frac{L_1}{L_1 + L_2}$$

The partial derivative of Q_{21} with respect to R_L is monotonic-increasing:

$$\frac{\partial(\Sigma x_{2i} - \Sigma x_{1i})}{\partial R_L} = (1-R_v)\sum \frac{(x_{2i}-x_{1i})^2}{z_i} \tag{14}$$

Since different equations are required for different phase combinations, the algorithm to find flow ratios must select the right equations. On the two-phase boundaries where either $R_1 = 0$, $R_2 = 0$, or $R_v = 0$, Eq. 10, 8 or 12 must be selected. In the three-phase region, Eqs. 8 and 10 are generally selected.

One challenge in using the formulation presented above is in the switching of governing equations. Algorithms based on this formulation search all regions sequentially with different governing equations to find the correct root. This approach is costly and it was very arbitrary until the work of Nelson (1987). Bunz et al. (1990) demonstrated Nelson's algorithm in their work.

Multiple searches required

The algorithm described in Nelson's article is likely the best

for this formulation. It apparently was used successfully for many years in the Shell Process Engineering Calculation System (SPECS) a sequential modular simulation system. In his algorithm to find flow ratios, Nelson divided the solution space into 7 points and regions. They are:

(1) vapor-phase only
(2) liquid-phase 1 only
(3) liquid-phase 2 only
(4) vapor-phase and liquid-phase 1
(5) vapor-phase and liquid-phase 2
(6) liquid-phase 1 and liquid-phase 2
(7) vapor-phase, liquid-phase 1, and liquid-phase 2.

With simple tests, solutions at points 1, 2, and 3 (or at vertices in (R_1, R_2) space) can be easily confirmed and the search terminated. If none of these is valid, numerical solutions are then obtained in each of the regions 4, 5, and 6 (or on boundary lines in (R_1, R_2) space). At each solution point on the boundary lines, simple tests are made to determine its validity before proceeding to the next region. A two-dimensional search method is finally used in region 7 if no valid solution has been obtained in the first 6 points and regions. Equations 8, 10, and 12 are used individually in regions 4, 5, and 6, respectively. Equations 8 and 10 are used in region 7.

Nelson argued convincingly that the first 6 cases are simple and should therefore be done first. Once it is determined that the solution is in region 7, considerable effort can then be spent to locate the three-phase solution. Since the algorithm always uses proper governing equations in all regions, failures in convergence must be related to numerical methods. Similar to others using this formulation, this algorithm requires many iterative calculations for trial solutions on boundaries.

Improved Formulations

Two methods have been found in this work to circumvent the problem of searching in multiple regions with different governing equations. Both are simple by design and yet have performed satisfactorily in numerical tests. The first one uses a set of tests at the beginning of the algorithm to select the suitable pair of equations for a given zone. The second method uses slightly modified equations to avoid this problem. They both share a general property that the governing equations are applicable from the interior of the search space to the boundaries. At the boundary, one of the equations is always applicable to locate the two-phase root, and the sign of the other determines the validity of that root.

Formulation using search zones

In the first method, the search space is divided into 6 zones as shown in Figure 1. When searching for a root in zones C and D, the search method may land on the boundaries $R_1 = 0$ or $R_v = 0$. Therefore, Eqs. 10 and 12 are used for the search. The selections are therefore as follows:

Mostly vapor:	Zones A, B:	Eqs. 8 & 10
Mostly liquid 2:	Zones C, D:	Eqs. 10 & 12
Mostly liquid 1:	Zones E, F:	Eqs. 8 & 12

Before starting the search for the root in the two-dimensional space, the algorithm identifies the zone where the root should be. In this procedure, we rely on the property of functions

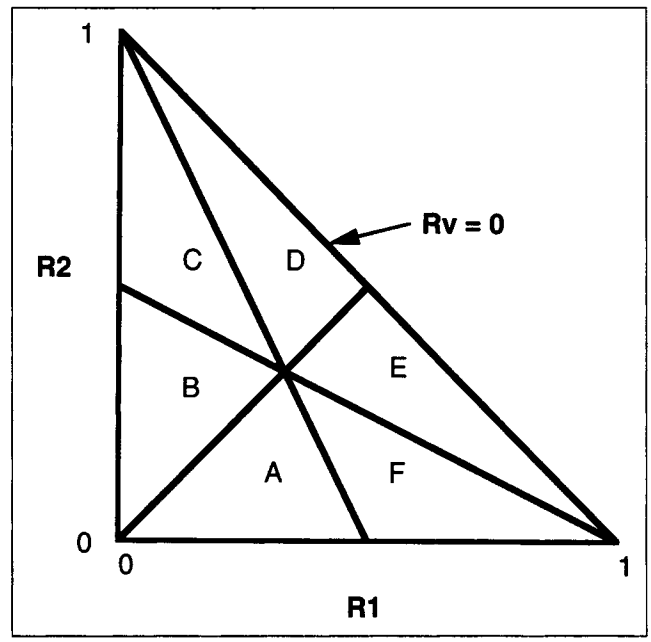

Figure 1. Search zones.

Q_{1v}, Q_{2v}, and Q_{21} being monotonic-decreasing on the respective boundary lines. If the value of Q_{1v} is positive at the midpoint of the R_1 axis, Q_{1v} can have a zero only to the right of the midpoint. Listed in the following table are all possible combinations of the signs of these functions at the midpoints of their respective boundary lines and the zone for the root to be in:

	Sign Combinations							
Q_{1v}	−	−	−	+	+	+	+	−
Q_{2v}	−	−	+	+	+	−	−	+
Q_{21}	−	+	+	+	−	−	+	−
Search Zone	A	B	C	D	E	F	?	?

The zones are selected according to the interception rule of domains. For example, if Q_{1v} at $(R_1 = 0.5, R_2 = 0)$ is negative, the root is assumed to lie inside zones A, B, or C. If Q_{2v} (0, 0.5) is negative, it is assumed to be in zones B, A, or F. If Q_{21} (0.5, 0.5) is negative, it is assumed to be in zones A, F, or E. The intercept of the three zones is zone A. Therefore, zone A is assumed if all three functions are negative at these respective midpoints.

The last two sign combinations do not give a clear indication where the root should be. Thus, we assume that in these two cases the root is close to the center of the search space. These are therefore combined with zones A and B.

The above analysis is shown only for completeness. The actual implementation of this logic is quite simple. The algorithm is as follows:

(1) Calculate Q_{1v}, Q_{2v}, and Q_{21} at the vertices: At (0, 0), if $Q_{1v} < 0$ and $Q_{2v} < 0$, the all-vapor point is the solution. At (1, 0), if $Q_{1v} > 0$ and $Q_{21} < 0$, the all-liquid-1 point is the solution. At (0, 1), if $Q_{2v} > 0$ and $Q_{21} > 0$, the all-liquid-2 point is the solution.

(2) Calculate Q_{1v}, Q_{2v}, and Q_{21} at the respective boundary midpoints: The solution is mostly vapor if $Q_{1v}(0.5, 0) < 0$ and

$Q_{2v}(0, 0.5)<0$. The solution is mostly liquid 1 if $Q_{1v}(0.5, 0)>0$ and $Q_{21}(0.5, 0.5)<0$. The solution is mostly liquid 2 if $Q_{2v}(0, 0.5)>0$ and $Q_{21}(0.5, 0.5)>0$. Otherwise assume mostly vapor.

(3) Use equations selected in step 2 and search for the root in the three-phase region. Note that the search may end at a solution on a boundary line with only one of the two selected equations satisfied.

In the following, we show that this formulation allows a solution at the boundary to be found through a search in the three-phase region. Therefore, this algorithm does not require trial solutions in the two-phase regions first. Furthermore, the selected equations are monotonic with respect to the selected coordinates in the designated zones.

If the solution is mostly vapor, we search in zones A and B for R_1 and R_2 such that Q_{1v} and Q_{2v} are zero. Equations 9 and 11 show that these two functions are monotonic with respect to their corresponding independent variables. Therefore, if the solution has no liquid 2, the search method should find the correct value of R_1 which makes Q_{1v} zero and should reach the boundary line, $R_2=0$, as a result of the monotonic characteristics of Q_{2v}. Figure 2 shows the search domain for this case.

If the solution is mostly liquid 1, we search in zones E and F for R_v and R_2 such that Q_{1v} and Q_{21} are zero. Rewriting Eq. 7 in terms of R_v and R_2, one obtains:

$$y_i=\frac{z_i}{R_v+\dfrac{(1-R_v-R_2)}{K_{1i}}+\dfrac{R_2}{K_{2i}}}; \quad i=1, \ldots, n$$

The partial derivatives of Q_{1v} and Q_{21} with respect to R_v and R_2 are:

$$\frac{\partial(\Sigma x_{1i}-\Sigma y_i)}{\partial R_v}=\sum\frac{(x_{1i}-y_i)^2}{z_i}$$

$$\frac{\partial(\Sigma x_{2i}-\Sigma x_{1i})}{\partial R_2}=-\sum\frac{(x_{2i}-x_{1i})^2}{z_i}$$

These equations show that the two functions are monotonic with respect to their corresponding independent variables. Therefore, if the solution has no liquid 2, the search method should find the correct value of R_v which makes Q_{1v} zero and should reach the boundary line, $R_2=0$, as a result of the monotonic characteristics of Q_{21}. Figure 3 shows the search domain for this case.

If the solution is mostly liquid 2, we search in zones C and D for R_v and R_1 such that Q_{2v} and Q_{21} are zero. Rewriting Eq. 7 in terms of R_v and R_1, one obtains:

$$y_i=\frac{z_i}{R_v+\dfrac{R_1}{K_{1i}}+\dfrac{(1-R_v-R_1)}{K_{2i}}}; \quad i=1, \ldots, n$$

The partial derivatives of Q_{2v} and Q_{21} with respect to R_v and R_1 are:

$$\frac{\partial(\Sigma x_{2i}-\Sigma y_i)}{\partial R_v}=\sum\frac{(x_{2i}-y_i)^2}{z_i}$$

$$\frac{\partial(\Sigma x_{2i}-\Sigma x_{1i})}{\partial R_1}=\sum\frac{(x_{2i}-x_{1i})^2}{z_i}$$

These equations show that the two functions are monotonic with respect to their corresponding independent variables. Therefore, if the solution has no liquid 1, the search method should find the correct value of R_v which makes Q_{2v} zero and should reach the boundary line, $R_1=0$, as a result of the monotonic characteristics of Q_{21}. Figure 4 shows the search domain for this case.

The algorithm for the first formulation was tested extensively using our collection of troublesome three-phase problems. Results were quite satisfactory. The additional time for evaluating three functions at three midpoints on the respective boundaries was negligible since these values helped locate the root.

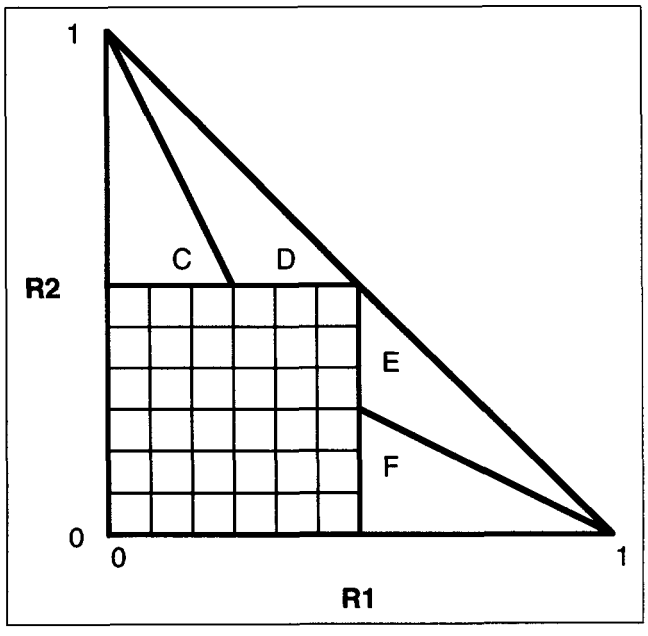

Figure 2. Search domain, mostly vapor.

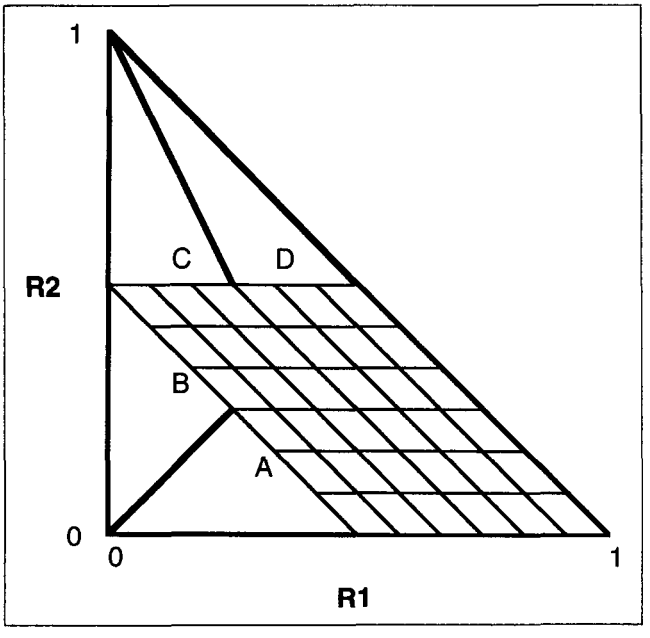

Figure 3. Search domain, mostly liquid 1.

Formulation using modified equations

The second formulation uses a single set of equations for the entire search space and hence further simplifies the logic of the search algorithm. A new equation is defined as follows:

$$Q_{xy} \equiv (1-R_L)\Sigma x_{2i} + R_L \Sigma x_{1i} - \Sigma y_i = 0. \tag{16}$$

The two equations used in the search space (R_v, R_L) are Eqs. 12 and 16. These equations can be shown to be valid in the entire search space except when $R_v = 1$.

At the solution point of Eq. 12 on the zero vapor line, S_1 and S_2 are both one. Q_{21} is zero but Q_{xy} equals $1 - S_v$. For constant values of R_L, the function Q_{xy} is monotonic-increasing with respect to R_v. Its value is positive for a solution with no vapor and negative if the vapor fraction must be determined.

$$\frac{\partial Q_{xy}}{\partial R_v} = \sum \frac{[(1-R_L)x_{2i} + R_L x_{1i} - y_i]^2}{z_i} \tag{17}$$

At the solution point of Eq. 16 on the line where $R_L = 1$ and $S_1 = S_v = 1$, Q_{21} equals $S_2 - 1$. Its value is negative for a solution with no liquid 2 and positive if the fraction of liquid 2 is required. A similar argument holds on the line where $R_L = 0$.

At the point where $R_v = 1$, R_L is not defined. This formulation is therefore valid for $R_v < 1$. In the implementation, we chose a value of $R_v = 0.9999999$ for dew point calculations and also as a limit for three-phase searches.

The algorithm is as follows:

(1) (Same as that for the first formulation.) Calculate Q_{1v}, Q_{2v}, and Q_{21} at the vertices: At (0, 0), the solution is all-vapor if $Q_{1v} < 0$ and $Q_{2v} < 0$. At (1, 0), the solution is all-liquid-1 if $Q_{1v} > 0$ and $Q_{21} < 0$. At (0, 1), the solution is all-liquid-2 if $Q_{2v} > 0$ and $Q_{21} > 0$.

(2) Use Eqs. 12 and 16 and search for the root in the three-phase space (R_L, R_V). Note that the search may end at a solution on a boundary line with only one of the two equations satisfied.

Three-Phase Search Algorithm

For the two formulations described above, there is no need to solve for two-phase solutions first. However, there is a need for a two-variable search algorithm that can take advantage of the monotonic properties of the functions and can move to the solution point on a boundary (that is, only one function is zero). The idea for the algorithm is similar to that for two-phase problems using the formulation of Rachford and Rice. With their formulation, if the search reaches the zero vapor point (that is, $R_v = 0$) and the search direction with respect to R_v is negative, the algorithm concludes that the mixture is below the bubble point and stops the search.

Most generalized packages for finding roots of two functions are not acceptable. A simple algorithm based on nested, single-variable search methods has been developed for the two formulations. A "nested" method solves the two-dimensional problem as two one-dimensional problems, an inner iterative loop to solve one problem nested within an outer iterative loop to solve the other. It can therefore benefit from the power of one-dimensional search algorithms such as that by Chien (1974). These algorithms are usually based on second- or higher-order

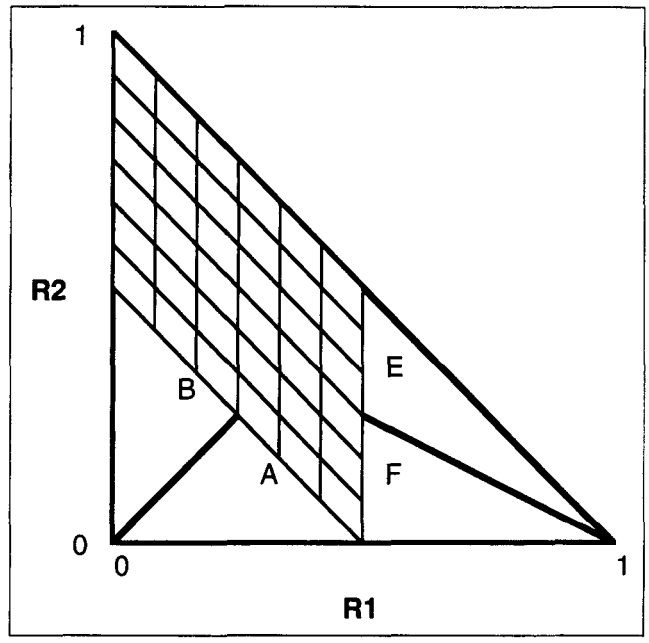

Figure 4. Search domain, mostly liquid 2.

polynomial approximations of functions to improve convergence.

For multidimensional searches, the gradient method is stable but slow near the solution; Newton's method is fast but can be very erratic for nonlinear functions. Some two-dimensional search algorithms perform orthogonal transformations at base points to discriminate against poor moves. However, since these methods take into account all partial derivatives simultaneously, whereas a "nested" method uses only diagonal terms of the partial derivatives, the requirements on functions to assure convergence are different.

In this work, we select system equations and coordinates to obtain monotonic behavior and benefit from the use of a "nested" method in speed, reliability, and simplicity of programming. For example, in cases where Q_{21} is identically zero, that is, R_L is indeterminate, the search is simply terminated.

In a nested method, the variables should be coupled to the functions in the following manner:

	Variable	Function
First formulation:		
zone A, B	R_2	Q_{2v}
	R_1	Q_{1v}
zone C, D	R_1	$-Q_{21}$
	R_v	$-Q_{2v}$
zone E, F	R_2	Q_{21}
	R_v	$-Q_{1v}$
Second formulation		
	R_L	$-Q_{21}$
	R_v	$-Q_{xy}$

The signs of functions are chosen so that their slopes are negative. While the outer variable is held constant, the function selected for the inner loop is always monotonic. In the outer loop, since the inner variable is not held constant, the function

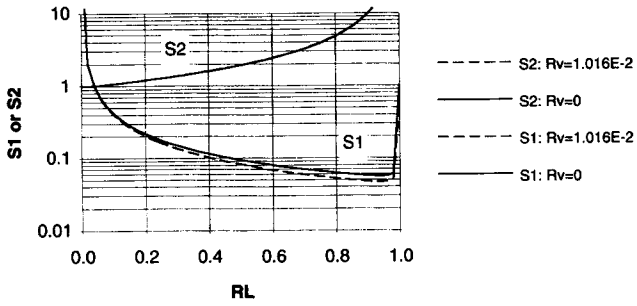

Figure 5. Sum of compositions, S_1 or S_2.

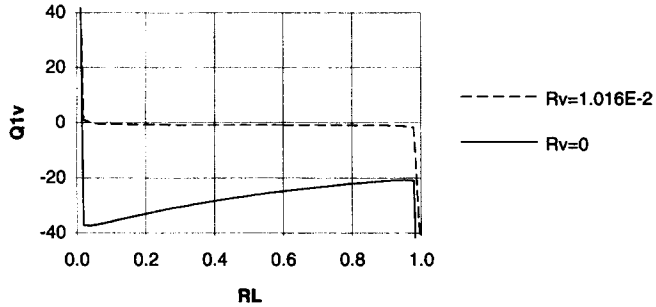

Figure 7. Sum of composition differences, Q_{1v}.

may not be monotonic. However, since the partial derivative of the outer function with respect to the outer variable is known to be negative, the search direction is never in doubt.

Special Considerations for a Nested Search

In a "nested" search, for a given value of the outer variable, a solution of the inner variable is obtained. The search path and hence the convergence is sensitive to the selection of functions, the coordinate system, their coupling, and the search order. Frequently, the inner search ends at a boundary. If the function coupled to the outer variable is not defined on this boundary, the overall search can fail. This problem is not as critical for a multidimensional simultaneous search method. Such a technique makes use of all partial derivatives and is therefore independent of the order of variables and the coordinates used.

Two examples are included to illustrate these points. Three-phase solutions of these examples are located close to the $R_2 = 1$ vertex. If a "nested" search method had used Q_{2v} and R_2 in the inner loop, Q_{1v} and R_1 in the outer loop, and a starting point of (0.5, 0.25), the following problem would have occurred: Q_{2v} is monotonic with respect to R_2 and would cause the inner loop to end on the $R_v = 0$ line at the start. However, on this line, Q_{1v} may not provide useful search information since it is not monotonic with respect to R_L.

$$\frac{\partial(\Sigma x_{1i} - \Sigma y_i)}{\partial R_L} = -(1 - R_v)\sum \frac{(x_{1i} - y_i)(x_{1i} - x_{2i})}{z_i} \qquad (15)$$

This means that for constant values of R_v, Q_{1v} may have multiple roots, and its slope may direct away from the solution. As mentioned previously, on the line $R_v = 0$, S_v may not be equal to one anywhere. Finding the roots of Q_{1v} on this line in the outer loop, that is, making S_1 equal to S_v, would not produce the approximate solution value for R_L.

Finding the root of Q_{21} on this line is useful in locating the solution since it makes $S_2 = S_1 = 1$. This can be shown by summing Eq. 13 from $i = 1$ to n and rearranging to get:

$$R_L S_1 + (1 - R_L)S_2 = \frac{1 - R_v S_v}{1 - R_v}$$

The righthand side is equal to one when R_v is zero. When Q_{21} is zero, or $S_1 = S_2$, they both equal one.

Example 1

The first example involving a ternary mixture has a three-phase solution at $R_1 = 0.03963$, $R_2 = 0.95021$, $R_v = 0.01016$ and has the following parameters:

$$\begin{array}{lll} z_1 = 0.04 & K_{11} = 0.02 & K_{21} = 100 \\ z_2 = 0.95 & K_{12} = 100 & K_{22} = 0.02 \\ z_3 = 0.01 & K_{13} = 2{,}000 & K_{23} = 4{,}000 \end{array}$$

From the K-values, it should be obvious that at equilibrium, component 1 should be mostly in liquid 1, component 2 in liquid 2, and component 3 in vapor. In Figures 5 and 6, we show the values of S_1, S_2, and S_v at $R_v = 0$ and 0.01016. On the zero vapor line, a root exists as shown in Figure 5, where Eqs. 5 and 6 (and hence Eq. 12) are satisfied. At this root, S_v is greater than 1, and according to the test in Nelson's algorithm, this root is correctly rejected.

Shown in Figures 7, 8, and 9 are values of Q_{1v}, Q_{2v}, and Q_{21} at the same constant R_v values. Obviously, Q_{1v} and Q_{2v} at $R_v = 0$ are not usable in locating the approximate root. Q_{1v} exhibits

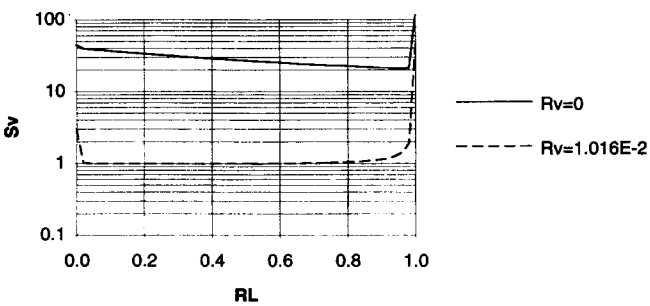

Figure 6. Sum of compositions, S_v.

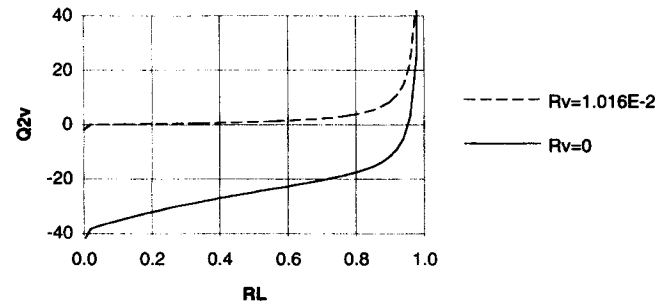

Figure 8. Sum of composition differences, Q_{2v}.

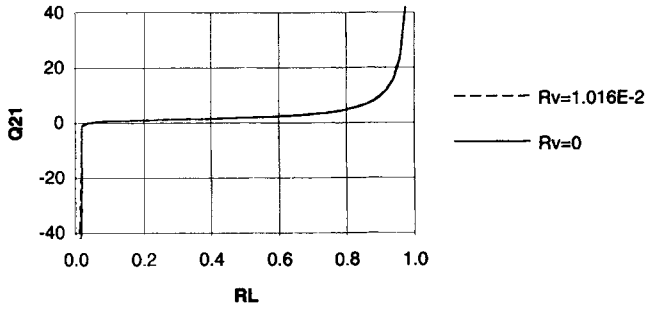

Figure 9. Sum of composition differences, Q_{21}.

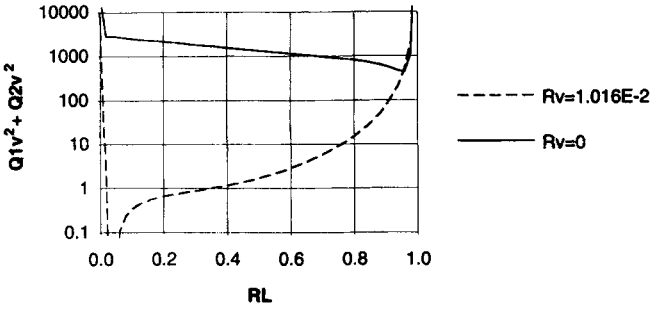

Figure 10. Sum of squared errors, $Q_{1v}^2 + Q_{2v}^2$.

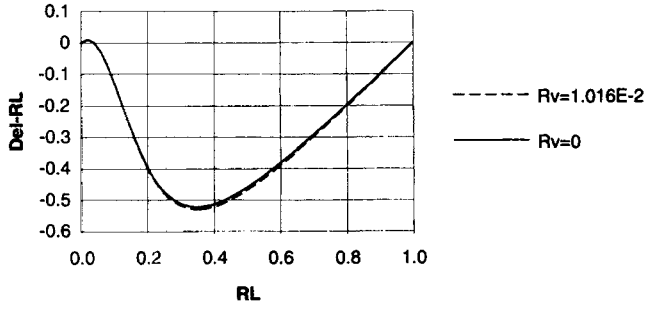

Figure 11. Newton's step sizes.

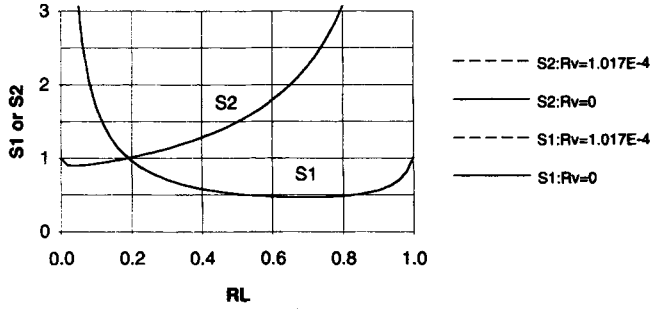

Figure 12. Sum of compositions, S_1 or S_2.

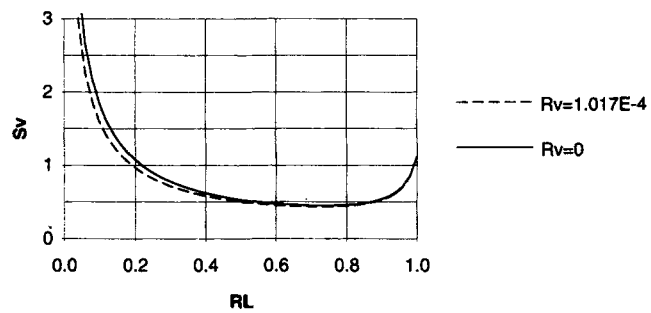

Figure 13. Sum of compositions, S_v.

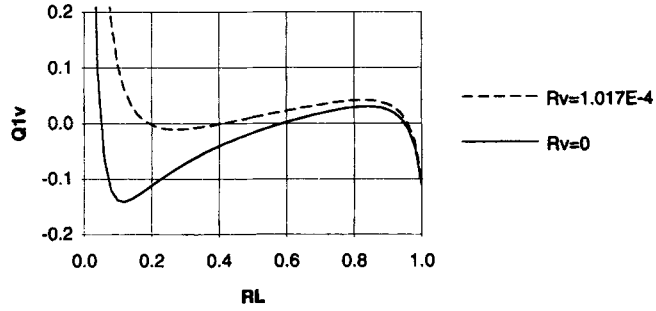

Figure 14. Sum of composition differences, Q_{1v}.

nonmonotonic behavior, and Q_{2v} displays a meaningless root at the opposite end of the axis. At this meaningless root, the values of S_1, S_2, and S_v are not one. Since values of S_v are significantly different at these two fixed values of R_v, the two roots of Q_{2v} swing from one end of the scale to the other. The function Q_{21} is monotonic and not changing for these R_v values. It is ideally suited for use in a "nested" search.

With multidimensional simultaneous search methods, results are much different. The sum of squared errors in Figure 10 shows that the search direction based on the gradient method at $R_v = 0$ would initially move away from the final R_L value. The direction would then be corrected once the base point is moved away from the boundary.

Figure 11 shows the changes in R_L calculated by Newton's method. Since these methods take into account partial derivatives in all directions, the large off-diagonal terms of the Jacobian matrix produce the correct directions of search. However, the steps near the two ends are very small. These are steps based on the intercepts with the axis of linear extrapolations of Q_{21}. (See Figure 9.) Since the function is very steep near the two ends, the step sizes become very small. This is one of the problems of linear methods rectified by the "nested" method.

Example 2

The second example is a simplified version of an actual process problem involving seven components. It has a three-phase solution at $R_1 = 0.1908$, $R_2 = 0.8091$, $R_v = 1.017e-4$ and has the following parameters:

$z_1 = 0.000129$	$K_{11} = 821.78$	$K_{21} = 13707$
$z_2 = 0.000607$	$K_{12} = 42.471$	$K_{22} = 894.08$
$z_3 = 0.003236$	$K_{13} = 6.4529$	$K_{23} = 0.462$
$z_4 = 0.15353$	$K_{14} = 0.61059$	$K_{24} = 70.872$
$z_5 = 0.023165$	$K_{15} = 0.37218$	$K_{25} = 8.9492$
$z_6 = 0.19711$	$K_{16} = 0.039947$	$K_{26} = 0.015288$
$z_7 = 0.622223$	$K_{17} = 1.362$	$K_{27} = 0.057418$

R_v is small but not zero because of the presence of gaseous

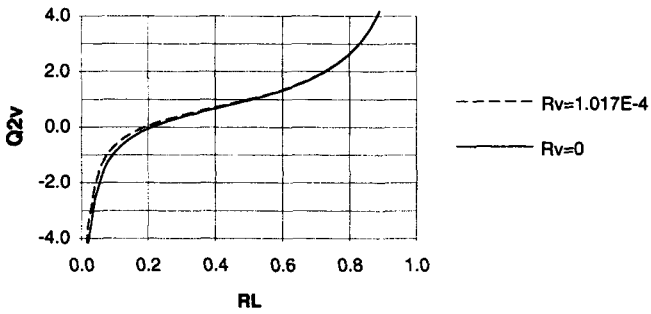

Figure 15. Sum of composition differences, Q_{2v}.

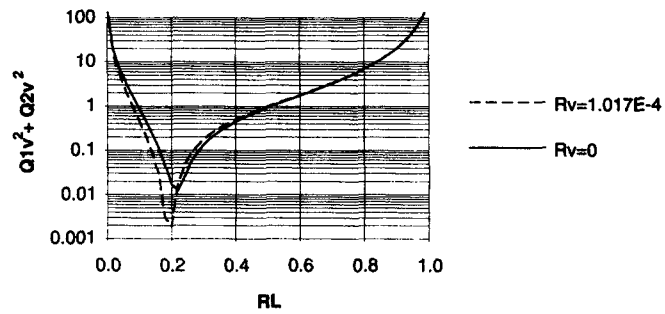

Figure 17. Sum of squared errors, $Q_{1v}^2 + Q_{2v}^2$.

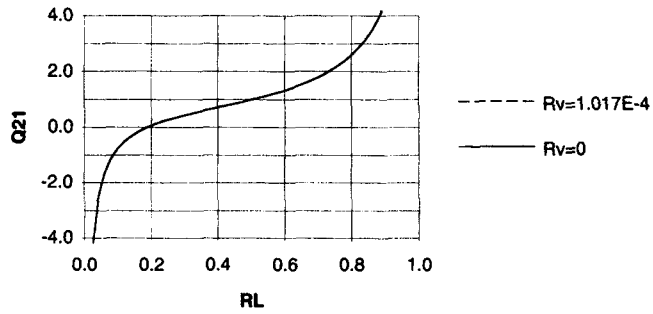

Figure 16. Sum of composition differences, Q_{21}.

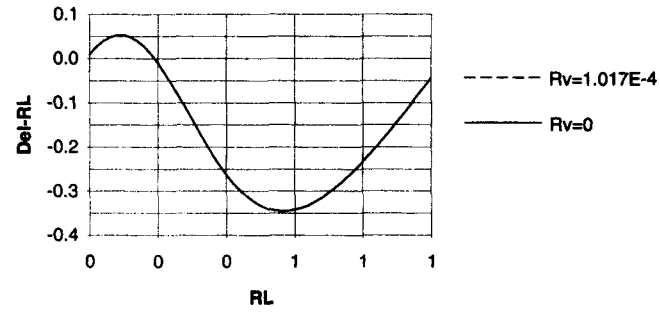

Figure 18. Newton's step sizes.

components 1 and 2. In Figures 12 and 13, values of S_1, S_2, and S_v at $R_v = 0$ and $1.017e-4$ are shown. On the zero vapor line, a root exists as shown in Figure 12 where Eqs. 5 and 6 (and hence Eq. 12) are satisfied. At this root, S_v is greater than 1, and according to the test in Nelson's algorithm, this root is correctly rejected.

Shown in Figures 14, 15, and 16 are values of Q_{1v}, Q_{2v}, and Q_{21} at the same R_v values. Q_{1v} exhibits multiple roots at $R_v = 0$ and is not usable in locating the approximate root. At these meaningless roots, the values of S_1, S_2, and S_v are not one. Again, the function Q_{21} is very stable and ideally suited for use in a "nested" search on the zero vapor line.

If we had used Q_{1v} and Q_{2v} in the nested search of the (R_1, R_2) space for this example problem, at some starting point, the slope of Q_{2v} in the inner loop would have directed the search to the $R_v = 0$ line. On this line, the search of the outer loop would have terminated at any one of the three roots. Only those starting points that end the search at the left-most root of Q_{1v} can find the correct three-phase solution successfully. Figure 17 shows the sum of squared errors, and Figure 18 shows the changes in R_L calculated by Newton's method.

Tests

Twelve test simulations for actual operating processes were used to check the validity of the above mentioned formulations. Both performed reliably. The second formulation is preferred and recommended because of its simplicity and its broader applicability. To facilitate the reproduction of our results, we include a sample problem with three different feed conditions that force the solutions to be in different zones. Converged results are given in Table 1.

Table 1. Results of Sample Problem with Three Different Feed Conditions

			Feed 1	Feed 2	Feed 3
i	K_{1i}	K_{2i}	z_i	z_i	z_i
1	0.02	100	0.03	0.04	0.95
2	100	0.02	0.02	0.95	0.04
3	2,000	4,000	0.95	0.01	0.01

R_1 = 1.022927E-2 3.963399E-2 9.504398E-1
R_2 = 2.156541E-4 9.502070E-1 3.962889E-2

It is clear from the K values that component 1 is mostly in the liquid-1 phase, component 2 mostly in liquid-2, and 3 is mostly in the vapor.

Notation

F = feed flow
H = enthalpy
K = vapor to liquid composition ratios
L = liquid flows
n = total number of components
P = pressure
Q = sum of composition differences
R_1 = ratio of liquid 1 flow to total flow
R_2 = ratio of liquid 2 flow to total flow
R_L = ratio of liquid 1 flow to total liquid flow
R_v = ratio of vapor flow to total flow
S = sum of compositions
T = temperature
V = vapor flow
x = liquid compositions in mole fractions
y = vapor compositions in mole fractions
z = feed compositions in mole fractions

Subscript

1 = liquid phase 1
2 = liquid phase 2
f = feed
i = component i
v = vapor phase

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