CHAPTER III

VAPOR-LIQUID EQUILIBRIUM CALCULATION

3.1 Flash Calculations

Flash calculation is a process calculation whereby a liquid passing through a valve undergoes a pressure drop sufficient to cause "Flashing" or partial vaporization, producing a two-phase stream of liquid and vapor in equilibrium. This calculation is also widely used to determine the phase condition of a stream of known composition, temperature and pressure.(14,35)

For a system containing a total of F moles of a feed mixture with overall composition given by the set of N mole fractions $z_i = z_1, z_2, z_3, \ldots, z_N$. Depending on temperature and pressure, the system may be entirely vapor. In this study, the interest is on state for which the system consists of liquid and vapor in equilibrium. Let L represents the number of moles of liquid, with mole fraction $x_i = x_1, x_2, \ldots, x_N$ and let V be the moles of vapor with mole fraction $y_i = y_1, y_2, \ldots, y_N$. The following material balance component must be satisfied

$$F = L + V \qquad (3.1)$$

A component material balance gives

$$z_i F = x_i L + y_i V \qquad (3.2)$$

where, by definition, the y are related to the x through the "K value", K

$$K_i = y_i / x_i \qquad (3.3)$$

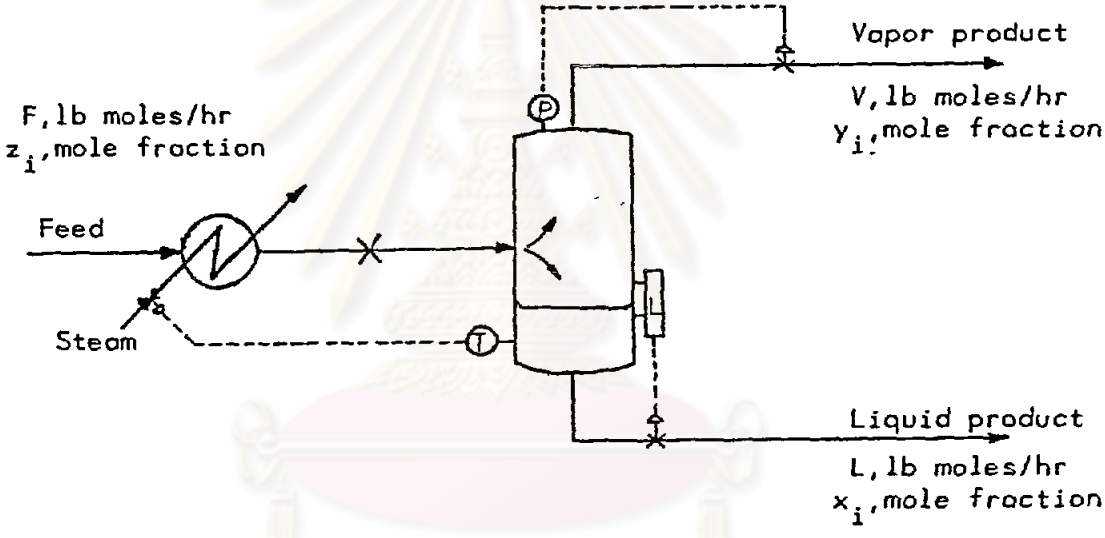

FIGURE 3.1 CONTINUOUS EQUILIBRIUM FLASH VAPORIZATION (14)

substitute Equation (3.1) and (3.3) into Equation (3.2) and eliminate either L or V from the equation, it gives

$$x_i = \frac{z_i}{(K_i-1)(V/F)+1} \qquad (3.4)$$

and

$$y_i = \frac{z_i(K_i-1)}{(K_i-1)(V/F)+1} \qquad (3.5)$$

but

$$\Sigma x_i = \Sigma y_i = 1.0$$

Then

$$\Sigma y_i - \Sigma x_i = 0.0$$

$$\sum_{i=1}^{N} \frac{z_i(K_i-1)}{(K_i-1)(V/F)+} = 0.0 = F(V/F) \qquad (3.6)$$

The Equation (3.6) is the criteria which yields a convergence function. In flash calculation the set z_i and $K_i = K_1, K_2, \ldots, K_N$ are presumed known. Then, a convergence method is applied to find a suitable value of (V/F) which makes F(V/F) = 0. The iterative variable (V/F) is bounded between 0 and 1, and the function is relatively linear in V/F.

For convenience, flash calculation are done on a computer, one must have a systematic iterative procedure for rapid convergence to the correct answer. The most widely employed computer methods for solving Equation (3.6) are the false position and the Newton's Raphson method. In this study, Newton's method was shosen for solving Equation (3.6). With this method, a predicted value of the

root of iteration (I+1) is computed from the recursion relation

$$(V/F)^{I+1} = (V/F)^{I} - \frac{F(V/F)^{I}}{F'(V/F)^{I}} \qquad (3.7)$$

where the derivative in Equation (3.7) is

$$F'(V/F)^{I} = \sum_{i=1}^{N} \frac{z_i(K_i-1)}{\{(K_i-1)(V/F)+1\}^2} \qquad (3.8)$$

The iteration can be initiated by assuming (V/F) = 0.5. Sufficient accuracy will be achieved by terminating the iteration when $\left|(V/F)^{I+1}-(V/F)^{I}/(V/F)^{I}\right| < \epsilon$, where ϵ is the tolerance of the system. Values of $(V/F)^{I+1}$should constrained to lie between 0 and 1. Then, if $(V/F)^{I}$ = 0.1 and $(V/F)^{I+1}$ is computed from Equation (3.7) to be 0.05, $(V/F)^{I+1}$ should be reset to, say, one half of the interval from $(V/F)^{I}$ to 0 or 1, whichever is closer to $(V/F)^{I+1}$ larger than 1, it will be reset to $(1+(V/F)^{I})/2.0$. One should check the existence of a valid root ($0< (V/F)< 1$) before returning to recalculate a correct root (V/F that gives F(V/F) = 0.0)

In any calculation of a simple equilibrium separation process, it is ususlly desirable to check first to make sure that two phases are present at equilibrium. This is done by performing bubble and dew point calculations.

3.2 Bubble and Dew Point Calculations

Bubble and dew point calculations are useful to determine saturation conditions for liquid and vapor streams, respectively. It is important to note that when vapor liquid is established, the vapor is at its dew point and the liquid is at its bubble point.

3.2.1 Bubble Point Calculations

In bubble point calculations, the liquid composition is known and either the temperature or pressure is fixed. The vapor phase composition and pressure or temperature of the system are unknown. The vapor phase is predicted by

$$y_i = K_i x_i \tag{3.9}$$

A precise indicator is the parameter V/F, which must lie between 0 and 1. If F(V/F) at V/F = 0 is greater than zero, the mixture is below its bubble point; and F(V/F) = 0, the mixture is at its bubble point.(12,14,25)

Let $x_i = z_i$ and $\sum_{i=1}^{N} x_i = \sum_{i=1}^{N} z_i = 1.0$, and V/F = 0, then

$$F(V/F) = F(0) = 1-\Sigma\, z_i K_i \tag{3.10}$$

The bubble point criterion, therefore, is

$$1 = \sum_{i=1}^{N} z_i K_i \tag{3.11}$$

This equation is useful for calculating bubble point temperature at a fixed pressure or bubble point preesure at a specified temperature.

3.2.2 Dew Point Calculations

Dew point calculations, in effect, are the opposite of bubble point calculations, the vapor phase composition is known and the liquid phase composition and the system temperature or pressure are to be calculated. The specified equation used in the dew point calculation is

$$x_i = y_i/K_i \tag{3.12}$$

If F(V/F) at V/F = 1 is less than zero, the mixture is above its dew point (superheated vapor). If F(V/F) = 1,the mixture is at its dew point.

Let $y_i = z_i$ and $\sum_{i=1}^{N} y_i = \sum_{i=1}^{N} z_i = 1.0$, and V/F = 1, then

$$F(V/F) = F(1) = \sum_{i=1}^{N} (z_i/K_i) - 1 \qquad (3.13)$$

Therefore, the dew point criterion is

$$\sum_{i=1}^{N} (z_i/K_i) = 1 \qquad (3.14)$$

3.2.3 Checking Phase Conditions for a Mixture (14)

By extending the reasoning involved in bubble and dew point calculations it can be seen that a mixture for which $\sum_{i=1}^{N} K_i x_i < 1$ will be a subcooled liquid, whereas if $\sum_{i=1}^{N} K_i x_i > 1$, the mixture must contain at least some vapor. Similarly, if $\sum_{i=1}^{N} (y_i/K_i) < 1$, a mixture will be a superheated vapor, and if $\sum_{i=1}^{N} (y_i/K_i) > 1$, the mixture must contain at least some liquid. Thus the following criteria can be set up to ascertain the phase condition of a mixture which potentially contains both vapor and liquid.

$\sum_{i=1}^{N} K_i x_i$	$\sum_{i=1}^{N} (y_i/K_i)$	Phase Condition
<1	>1	Subcooled liquid
=1	>1	Saturated liquid
>1	>1	Mixed vapor and liquid
>1	=1	Saturated vapor
>1	<1	Superheated vapor

In another way, it can be checked that F(V/F) is positive at V/F = 0 and negative at V/F = 1, then the two phase exist. If F(V/F) is negative at (V/F) = 0, a mixture will be a subcooled liquid. On the other hand, if F(V/F) is positive at V/F = 1, a mixture will be a superheated vapor.

3.3 Method of Calculation

A trial and error solution of an implicit equaton involving a single variable consists of assuming value for the unknown variable until a value is found which satisfies the equation. An equation involving a single variable x can be written as

$$f(x) = 0$$

where f(x) is the function resulting from putting all terms of the equation on the left hand side. In a trial and error or iterative, solution successive values of x are assumed according to a systematic plan until a value of x which causes a f(x) to be zero is found.

In practical computing, there is only a discrete set of numbers to try as possible zeros, and none of these may happen to produce exactly zero for f(x). We shall therefore seek a pair of numbers, x_1, x_2, which are "closed to each other" and such that $f(x_1)$ and $f(x_2)$ have opposite signs (or in rare case one of them may be zero).

In practice, because of the random effects of the roundoffs which occur in the function evaluation of f(x), we usually have not a single change of sign, but a short sequence of consecutive numbers which gives a sequence of changes in sign for f(x). Although in principle this could be confused with a sequence of distinct zeros, in prctice there is little trouble with this effect provided we can form a reasonable estimate of the size of the roundoff error made during the function evaluation. Roundoff troubles are bound to occur in the problem that there is almost an exact cancellation between the positive terms and the negative

terms that occur in the function evaluation process. Suitable systematic plan for this finding a solution are called convergence method. We consider here the Newton Raphson method of convergence.

3.3.1 Newton Raphson Method (Newton's Method of Convergence)

This method is very useful for improving a first approximation of a root of an equation of the form $f(x) = 0$, which might have been obtained by the search method, by an approximate graph of the function, or by some other means.

Consider the graph of $f(x)$ versus x, shown in Figure 3.1, and assume that x is the first approximation of a root. If we draw a tangent line to the curve at $x = x_n$, the tangent line will intersect that x axis at a value x_{n+1}, which is an improved approximation to the root. It can be seen Figure 3.2 that the slope of the tangent line is

$$f'(x_n) = \frac{f(x_n}{x_n - x_{n+1}} \tag{3.16}$$

from which

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)} \tag{3.17}$$

The value of the function and the value of the derivative of the function are determined at $x = x_n$, and the approximation to the root, x_{n+1}, is obtained by using Equation (3.17). The same procedure is repeated, with the new approximation, to get a still better approximation to the root. This continues until successive values of the approximation root differ by less than a prescribed

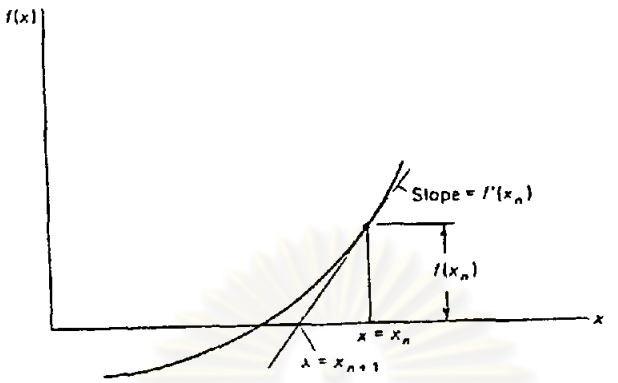

FIGURE 3.2 NEWTON-RAPHSON METHOD (42)

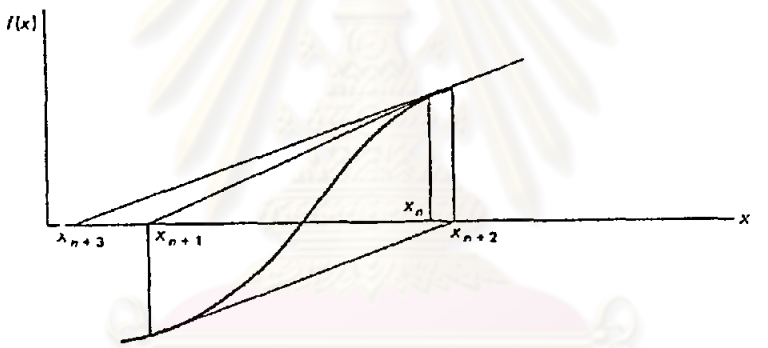

FIGURE 3.3a A CASE OF NO CONVERGENCE (42)

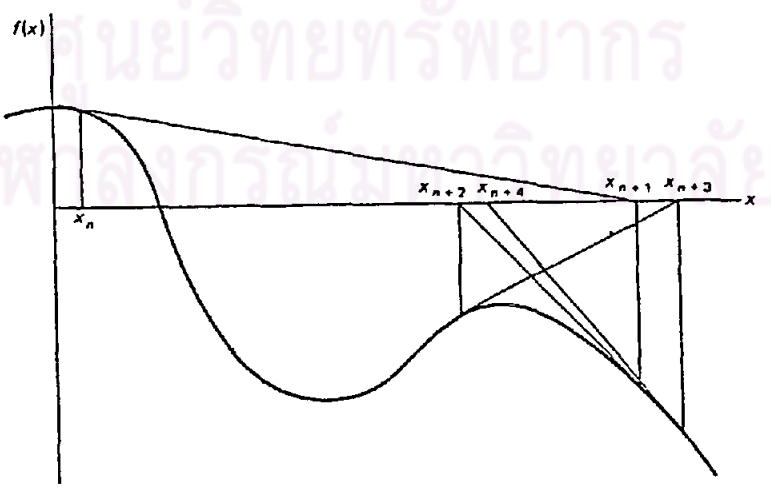

FIGURE 3.3b A SECOND CASE OF NO CONVERGENCE (42)

small epsilon (ε) which controls the allowable error in the root, or until the value of the function becomes less than some prescribed small value.

The Newton Raphson method is widely used in practice because of its generally rapid convergence. However, there are cases in which convergence does not occur. One such example is shown in Figure 3.3a where f'(x) changes sign near the root. A second case in which canvergence may not occur is llustrated in figure 3.3b. In this example, the initial approximation to the root was not sufficiently close to the true value, and the tangent to the cureve for x has a very small slope, resulting in x being for the right where a local maximum in the curve causes the difficulty (oscillation about the local maximum). Other functions could be illustrated in which there is a jump to root other than the one nearest to the first approximation. These difficulties can be avoided by having the initial approximation sufficiently close to the root value, but sometimes this is not possible.

As we have seen, the Newton Raphson method required the differentiation of the function. If the derivative of the function is very complicated, it may be advantageous to suitable a finite difference approximation of the derivative for the actual derivative. (11,15,41)

3.2.2 Desirable Characteristics

In devising or choosing a convergence method for a particular calculation, one should seek several desirable characteristics :

1. The convergence method should lead to the

desired root of the equation. If the equation has multiple root, the convergence should lead reliably to the particular root in question.

2. The convergence method should be stable; it should approach the root asymtotically or in a well damped oscillating fashion, rather than developping large oscillations of successive values of the trial variable.

3. The convergence method should lead rapidly to the desired value. Many iterations or many computations per iteration will require more computer time. This speed of convergence criterion is particularly important when the equation is involved in a subroutine which must be solved many times in the course of a main calculation.

4. Iterations should be avoided wherever possible. For example, it is usually better to solve a cubic equation by an algebraic approach than by an iterative solution.

5. If there is any doubt whether convergence has been achieved, it is desirable to surround the answer, i.e., come at it from both sides. (14)

3.3.3 Initial Estimates and Tolerance

In order to implement a convergence method for the computer it is necessary to provide some procedure for obtaining an initial estimate x and to indicate the tolerance, which is the allowable error in f(x) within which the calculation will be stopped. The initial estimate can be selected in one of two ways : one can specify a particular value for x which is known to be in a region such that the convergence method will lead to the converged

solution in a straightforward manner, or if the calculation is being repeated for a number of different values of other variables included in $f(x)$, one can use the last previous converged value of x as the first estimate for the next calculation.

The tolerance should be selected so that x will be found within the desired degree of precision but should not be low enough to require an unnecessarily large number of iterations. If there is a possibility that the specified tolerance is too large, it is useful to surround the answer by coming at it from both sides. (14)