# Chapter IV

## Algorithm and Calculation

### Computation Procedure for Three-Phase Flash by Equation of State

Fugacity coefficients,activity coefficients and other thermodynamic properties can be calculated by equation of state that are applicable to both liquid and vapor phases. In this case use equation of state to calculate all parameter is shown step by step as follows.

1. At the given T,P and fixed $z_i$,initial estimate of $x_i'$,$x_i''$,$y_i$ are made.

2. Calculate $\phi_{iv}$,$\phi_{iL}'$,$\phi_{iL}''$ from equation of state.

3. Calcalate $K_i'$,$K_i''$ from relation $K_i' = \phi_{iL}'/\phi_{iv}$,$K_i''=\phi_{iL}''/\phi_{iv}$.

5. Iteratively calculate $u_1$,$u_2$ from equation 2.32.

6. Calculate $x_i'$,$x_i''$,$y_i$ from equation 2.17,2.18,2.14.

7. Compare estimated and calculated values of $x_i'$,$x_i''$,$y_i$ ,if converged then print result,if not start step 1. The algorithm for calculation can be shown in figure 4.2.

### The Criteria for Inital Estimate in Three-Phase Flash System

In order to estimate suitable starting compositions which used in three-phase calculation procedure,it is

Table 4.1 Values of $Q_1$, $Q_2$ and $Q_1-Q_2$ at the vertices

| $U_1$ | $U_2$ | $Q_1(U_1,U_2)$ | $Q_2(U_1,U_2)$ | $Q_1(U_1,U_2)-Q_2(U_1,U_2)$ |
|---|---|---|---|---|
| 0 | 0 | $\Sigma z_i/K_i'-1$ | $\Sigma z_i/K_i''-1$ | $\Sigma z_i/K_i'-\Sigma z_i/K_i''$ |
| 1 | 0 | $1-\Sigma z_i K_i'$ | $\Sigma z_i K_i'/K_i''-\Sigma z_i K_i'$ | $1-\Sigma z_i K_i'/K_i''$ |
| 0 | 1 | $\Sigma z_i K_i''/K_i'-\Sigma z_i K_i''$ | $1-\Sigma z_i K_i''$ | $\Sigma z_i K_i''/K_i'-1$ |

useful to understand the behavior of three-phase system before estimated compositions in individual phase be started.

If the function $Q_1(u_1,u_2)$, $Q_2(u_1,u_2)$ and $Q_1(u_1,u_2)-Q_2(u_1,u_2)$ at the vertices and along the adges of the triangular domain of figure 4.1. are evaluated and shown in table4.1 for $Q_1$, $Q_2$, $Q_1-Q_2$. Under normal circumstances, in three-phase region, it is found that:

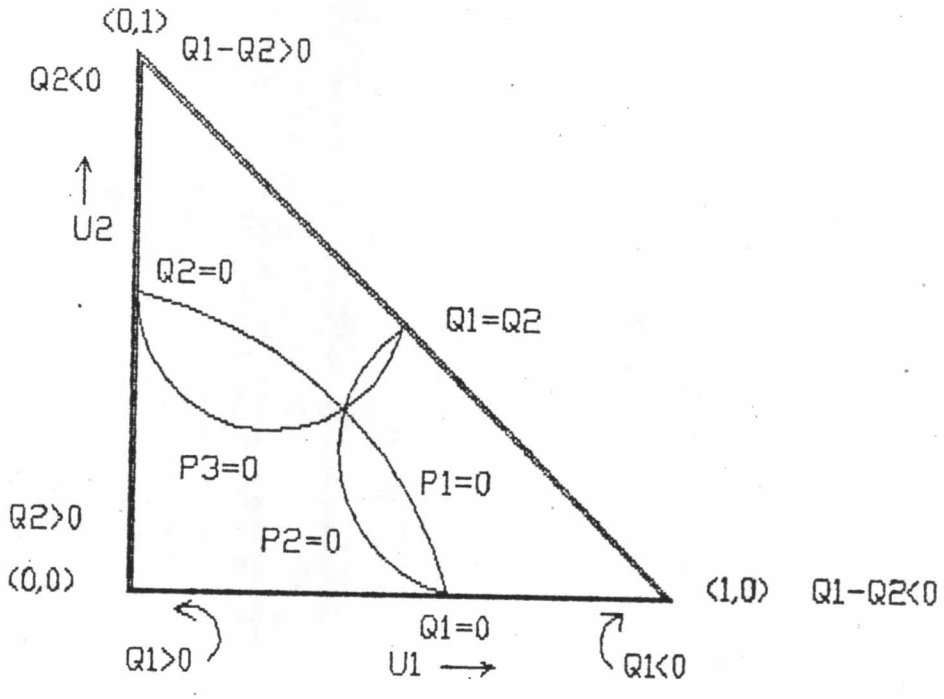
$$\sum_{i=1}^{c} z_i K_i' > 1 \qquad \sum_{i=1}^{c} z_i/K_i' > 1 \qquad 4.1a$$

$$\sum_{i=1}^{c} z_i K_i'' > 1 \qquad \sum_{i=1}^{c} z_i/K_i'' > 1 \qquad 4.1b$$

$$\sum_{i=1}^{c} z_i K_i'/K_i'' > 1 \qquad \sum_{i=1}^{c} z_i K_i''/K_i' > 1 \qquad 4.1c$$

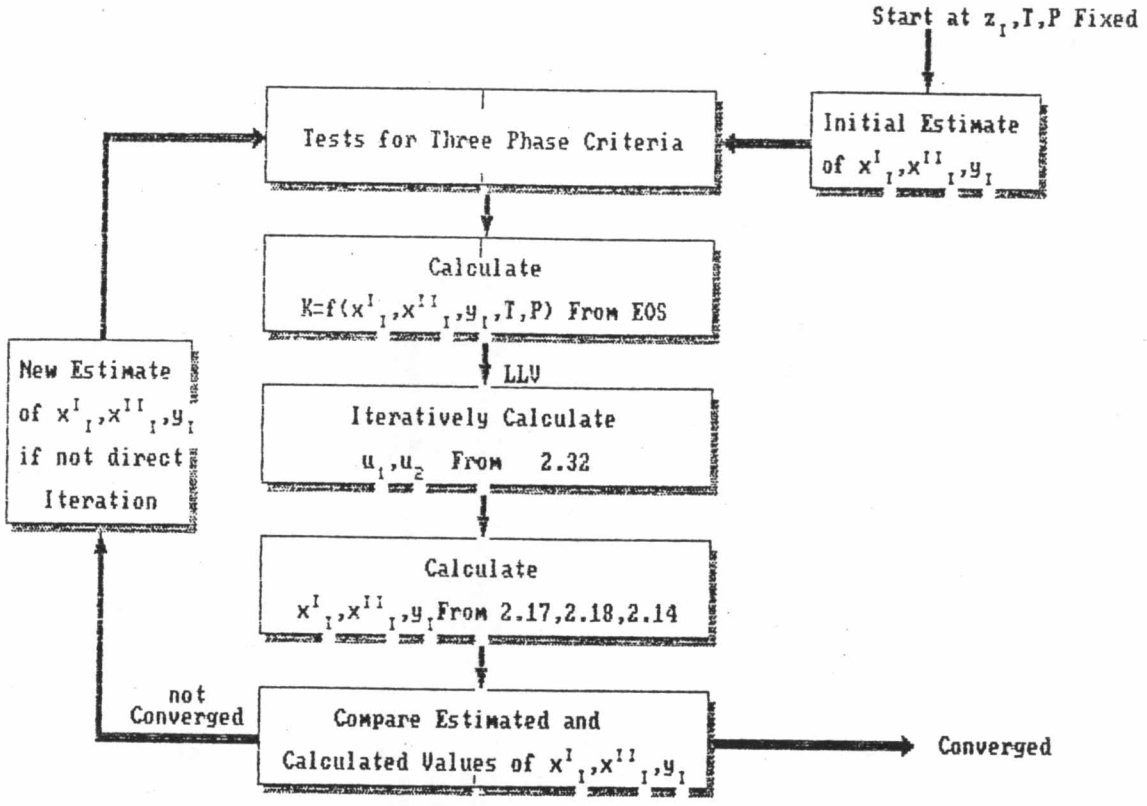
These relations are not violate, but if they are not

satisfied vapor- and liquid phase 1 can not coexist in the absence of a second liquid-phase.The relations in inequalities(4.1a-4.1c)lead to the normal behavior of the function $Q_1$,$Q_2$ and $Q_1$-$Q_2$ shown in figure 4.1. The functions $Q_1(0,0)$is normally positive and $Q_1(1,0)$is normally negative.$Q_1$ must then be zero somewhere along the $u_1$-axis.Equations (2.21) and (2.22) indicate that at that point $P_1(u_1,0)$ and $P_2(u_1,0)$ are zero as well.Similar




Location of the zero of P1,P2 and P3 for normal three-phase behavior

**Figure 4.1**




Algorithm for Isothermal Three-Phase Equilibrium Calculations

Figure 4.2

considerations govern the behavior of $Q_2(0,u_2)$ along the $u_2$-axis and $Q_1(u_1,1-u_1)-Q_2(u_1,1-u_1)$ along the diagonal edge. Consider a system described by the point $Q_1(u_1,0)=0$ along the $u_1$-axis as shownin figure.

The relations in inequalities(4.1a-4.1c) are treated for suitable starting composition in algorithm of three-phase flash.Because in the step of initial estimate of compositions in individual phase, $x_1'$,$x_1''$,$y_1$ and from relation of $K_1'=y_1/x_1'$, $K_1''=y_1/x_1''$ and fixed feed $z_1$.If these criteria are not violated the caculations procedure are continued,in the other hand the criteria are not satisfied re-estimation will be provided.

## Example Calculation for Soave Redlich Kwong Equation of State

### 1. Calculation Parameters for Pure Component

**Table 4.2 Initial Parameters T=298.15 K P=48.95 bar**

| Component | $T_c$ | $P_c$ | w | $y_1$ | $x'_1$ | $x''_1$ | $z_1$ |
|---|---|---|---|---|---|---|---|
| Methane | 190.40 | 46.00 | 0.0110 | 0.0828 | 0.0325 | 0.0357 | 0.0577 |
| Ethane | 305.40 | 48.82 | 0.0940 | 0.9171 | 0.8940 | 0.9572 | 0.9154 |
| n-Docosane | 770.00 | 11.02 | 0.8680 | 0.0001 | 0.0735 | 0.0071 | 0.0269 |

calculate K from relations

$$K_i' = y_i / x_i' \qquad K_i'' = y_i / x_i''$$

**Table 4.3 Initial K-values**

| Component | $K_i'$ | $K_i''$ |
|---|---|---|
| Methane | 2.5477 | 2.3193 |
| Ethane | 1.0214 | 0.9659 |
| n-Docosane | 0.0014 | 0.0141 |

$$\sum_{i=1}^{c} z_i K_i' = 1.0860 \qquad \sum_{i=1}^{c} z_i / K_i' = 20.6865$$

$$\sum_{i=1}^{c} z_i K_i'' = 1.0112 \qquad \sum_{i=1}^{c} z_i / K_i'' = 2.8902$$

$$\sum_{i=1}^{c} z_i K_i' / K_i'' = 1.0461 \qquad \sum_{i=1}^{c} z_i K_i'' / K_i' = 1.1860$$

We have found that inequalities in (4.1a-4.1c) are not violated and may be considered that initial estimated composition of three-phase system suitable starting compositions and the functions $Q_1$ and $Q_2$ can run to the point of zero along the edges of the triangular domain of figure 4.1,then continued to step 2.

calculation pure parameter:

$$a_{ii} = \alpha(T)(0.42748 R^2 T_{ci}^2 / p_{ci})$$

where $\alpha_i(T) = [1+m_i(1-\sqrt{T/T_{ci}})]^2$

$m_i = 0.480+1.574w_i-0.176w_i^2$

and $b_{ii} = 0.08664RT_{ci}/p_{ci}$

$A_i = a_{ii}P/R^2T^2$

$B_i = b_{ii}P/RT$

**Table 4.4 Parameters for pure component**

| Component | $a_{ii}$ | $b_{ii}$ | $A_i$ | $B_i$ | $m_i$ |
|---|---|---|---|---|---|
| Methane | 1.7343 | 0.0294 | 0.1420 | 0.0589 | 0.4973 |
| Ethane | 5.5737 | 0.0444 | 0.4565 | 0.0890 | 0.6264 |
| n-Docosane | 419.6447 | 0.4964 | 34.3666 | 0.9939 | 1.7136 |

compressibility of pure component can be calculated from:

$$Z^3 - Z^2 + Z(A_i - B_i - B_i^2) - A_iB_i$$

**2. Calculation Compressibility Factor and Mixture Parameter**

Where a and b in a mixture are found from:

Vapor phase: $a = \sum_i \sum_j y_i y_j a_{ij}$

$b = \sum_i \sum_j y_i y_j b_{ij}$

Liquid I:

$$a = \sum_{i}^{c}\sum_{j}^{c} x_i' x_j' a_{ij}$$

$$b = \sum_{i}^{c}\sum_{j}^{c} x_i' x_j' b_{ij}$$

Liquid II:

$$a = \sum_{i}^{c}\sum_{j}^{c} x_i'' x_j'' a_{ij}$$

$$b = \sum_{i}^{c}\sum_{j}^{c} x_i'' x_j'' b_{ij}$$

$$A = aP/R^2T^2$$

$$B = bP/RT$$

$$Z^3-Z^2+Z(A-B-B^2)-AB \qquad (4.2)$$

In these calculations,the compressibility factor Z is obtained from equation(4.2).The largest root of equation (4.2)is used to evaluate gas-phase fugacity coefficients;the smallest root of equation(4.2)is used to evaluate liquid-phase fugacity coefficients. Newton-Raphson calculational technique with initial estimates of the compressibility factor being set at 1 for the gas phase and 0 for the liquid phase.

$$f = Z^3-Z^2+(A-B-B^2)-AB$$

$$f' = 3Z^2-2Z+(A-B-B^2)$$

$$Z_{m+1} = Z_m - f(Z_m)/f'(Z_m) \qquad m=0,1,2...$$

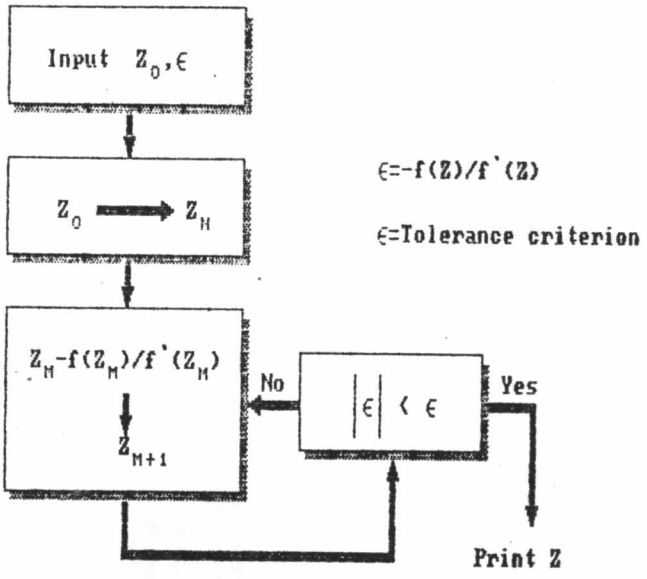



**Figure 4.3**

for vapor phase A=0.4243 and B=0.0866,set initial compressibility factor at 1 then

| f/f' | Z |
|---|---|
| -0.2206 | 0.7794 |
| -0.1459 | 0.6335 |
| -0.0950 | 0.5385 |
| -0.0590 | 0.4795 |
| -0.0318 | 0.4477 |
| -0.0114 | 0.4363 |
| -0.0015 | 0.4348 |
| -0.0000 | 0.4348 |
| 0.0000 | 0.4348 |

Table 4.5 Parameters for Mixture

| Phase | a | b | A | B | Z |
|---|---|---|---|---|---|
| Vapor | 5.1813 | 0.0432 | 0.4243 | 0.0866 | 0.4347 |
| Liquid I | 13.3889 | 0.0772 | 1.0958 | 0.1545 | 0.2284 |
| Liquid II | 6.0137 | 0.0471 | 0.4925 | 0.0943 | 0.2057 |

compressibility factor for vapor phase is 0.4347. The compressibility factor for liquid I and liquid II can becalculated in the same procedure but set initial compressibility factor at 0, in this case compressibility factor for liquid I and liquid II are 0.2284,0.2057 respectively.From relation of

$$v = ZRT/P$$

molar volume can be calculated

Table 4.6 Molar Volume of Mixture(l/g.mol)

| Vapor | L1-phase | L2-phase |
|---|---|---|
| 0.2171 | 0.1141 | 0.1027 |

3. Calculation Fugacity Coefficients of Mixture

Parameter from above can used for calculate fugacity coefficient of component in the mixture from following relation

$$\ln\phi_i = (Z-1)B_i/B-\ln(Z-B)-(A/B)[2A_i^{0.5}/A^{0.5}-B_i/B]\ln((Z+B)/Z)$$

and the appropriate phase composition and compressibility factor are used.After that K-value can be calculaed from

$$K_i' = \phi_{iL}'/\phi_{iv} = y_i/x_i'$$
$$K_i'' = \phi_{iL}''/\phi_{iv} = y_i/x_i''$$

and result of calculation show follow:

Table 4.7 **Fugacity Coefficients of Mixture**

| Phase | $\phi_{iv}$ | $\phi_{iL}'$ | $\phi_{iL}''$ | $K_i'$ | $K_i''$ |
|---|---|---|---|---|---|
| Methane | 1.2791 | 2.9133 | 2.2541 | 2.2776 | 1.7622 |
| Ethane | 0.6329 | 0.6319 | 0.6127 | 0.9984 | 0.9681 |
| n-docosane | 0.0000 | 0.0000 | 0.0000 | 0.0002 | 0.0008 |

**4. Calculation Fraction of Feed in Liquid Phases**

The procedure for search the values of $u_1$,$u_2$ must be performed,the result of this procedure are shown and Newton-Raphson method be used for finding and convergence is

declared when $Q_1$,and $Q_1$ are zero or within tolerance.

$$\begin{vmatrix} u_1 \\ \\ u_2 \end{vmatrix}_{m+1} = \begin{vmatrix} u_1 \\ \\ u_2 \end{vmatrix}_m - \begin{vmatrix} dQ_1/du_1 & dQ_1/du_2 \\ \\ dQ_2/du_1 & dQ_2/du_2 \end{vmatrix}_m^{-1} \begin{vmatrix} Q_1 \\ \\ Q_1 \end{vmatrix}_m$$

| $Q_1$ | $Q_2$ | $u_1$ | $u_2$ |
|---|---|---|---|
| 0.0009 | -0.0005 | 0.4276 | 0.3724 |
| 0.0001 | 0.0000 | 0.4288 | 0.3702 |
| 0.0000 | 0.0000 | 0.4288 | 0.3702 |
| 0.0000 | 0.0000 | 0.4288 | 0.3702 |
| 0.0000 | -0.0000 | 0.4288 | 0.3702 |

The root of these calculation are $u_1 = 0.4288$ and $u_2 = 0.3702$.

### 5. Calculation Mole Fraction and K-values

From relations of:

$$F = V+L'+L''$$

$$1 = \alpha+u_1+u_2$$

$$\alpha = V/F$$

$$\beta = L'/(L'+L'')$$

$$u_1 = L'/F$$

$$u_2 = L''/F$$

compositions in each phase can be calculated from

$$x_i' = z_i/(\alpha K_i' + (1-\alpha)(\beta + (1-\beta)K_i'/K_i''))$$

$$x_i'' = z_i/(\alpha K_i'' + (1-\alpha)(\beta K_i''/K_i' + 1-\beta))$$

$$y_i = K_i' x_i' = K_i'' x_i''$$

and the result after calculate can be shown below:

**Table 4.8 Mole Fraction and K-values**

| Phase | Vapor | Liquid I | Liquid II | $K_i'$ | $K_i''$ |
|---|---|---|---|---|---|
| Methane | 0.0962 | 0.0422 | 0.0546 | 2.2776 | 1.7622 |
| Ethane | 0.9038 | 0.9052 | 0.9336 | 0.9984 | 0.9681 |
| n-docosane | 0.0000 | 0.0525 | 0.0118 | 0.0002 | 0.0008 |

## Example Calculation for Equation of state of Harmens & Knapp

Calculations of three-phase flash by Harmens & Knapp equation of state and procedure in these calculation follow in the same way as SRK equation of state.

### 1. Calculation Parameters for Pure Component

**Table 4.9 Initial Parameters at T=298.15 K P=48.95 bar**

| Component | $T_c$ | $P_c$ | w | $y_i$ | $x'_i$ | $x''_i$ | $z_i$ |
|---|---|---|---|---|---|---|---|
| Methane | 190.40 | 46.00 | 0.0110 | 0.0878 | 0.0325 | 0.0357 | 0.0577 |
| Ethane | 305.40 | 48.82 | 0.0940 | 0.9121 | 0.8930 | 0.9582 | 0.9154 |
| n-Docosane | 770.00 | 11.02 | 0.8680 | 0.0001 | 0.0745 | 0.0061 | 0.0269 |

calculation pure parameter(Table 2.4):

$$a_{ii} = \alpha(T_r)\Omega_a R^2 T_c^2 / P_c$$

$$b_{ii} = \Omega_b R T_c / P_c$$

$$c_{ii} = 1+(1-3\zeta)/\beta\zeta$$

**Table 4.10 Parameters for pure component**

| Component | $a_{ii}$ | $b_{ii}$ | $c_{ii}$ |
|---|---|---|---|
| Methane | 1.7428 | 0.0279 | 1.4788 |
| Ethane | 5.8828 | 0.0410 | 1.7280 |
| n-Docosane | 585.8807 | 0.3947 | 3.2970 |

**2. Calculation Compressibility Factor and Mixture Parameters**

Where a,b and C in a mixture are found from:

Vapor phase:
$$a = \sum_i \sum_j y_i y_j a_{ij}$$

$$b = \sum_i \sum_j y_i y_j b_{ij}$$

$$C = \sum_i \sum_j y_i y_j c_{ij}$$

Liquid I:
$$a = \sum_i \sum_j x_i' x_j' a_{ij}$$

$$b = \sum_{i}^{c}\sum_{j}^{c} x_i' x_j' b_{ij}$$

$$C = \sum_{i}^{c}\sum_{j}^{c} x_i' x_j' c_{ij}$$

Liquid II:

$$a = \sum_{i}^{c}\sum_{j}^{c} x_i'' x_j'' a_{ij}$$

$$b = \sum_{i}^{c}\sum_{j}^{c} x_i'' x_j'' b_{ij}$$

$$C = \sum_{i}^{c}\sum_{j}^{c} x_i'' x_j'' c_{ij}$$

$$A = aP/R^2T^2$$

$$B = bP/RT$$

$$Z^3-(1+B-CB)Z^2+(A+(1-C)B^2-CB^2-CB)Z-AB-(1-C)B^2-(1-C)B^3 = 0$$

**Table 4.11 Parameters for Mixture**

| Phase | a | b | c | Z |
|---|---|---|---|---|
| Vapor | 5.4316 | 0.0399 | 1.7063 | 0.4184 |
| Liquid I | 16.0970 | 0.0670 | 1.8368 | 0.1779 |
| Liquid II | 6.3446 | 0.0427 | 1.7287 | 0.1760 |

Table 4.12 Molar Volume of Mixture(l/g.mol)

| Vapor | L1-phase | L2-phase |
|---|---|---|
| 0.2090 | 0.0888 | 0.0879 |

### 3. Calculation Fugacity Coefficients of Mixture

Parameter from above can used for calculate fugacity coefficient of component in the mixture from following relation:

$$\ln\phi_i = (Z-1)b_i/b-\ln(Z-B)+A(b_i/b-\delta_i)L/[B\sqrt{(C^2-4(1-C))}]$$

$$L = \ln\{(2Z+[B(C+\sqrt{(C^2-4(1-C))}]/(2Z+[B(C-\sqrt{(C^2-4(1-C))}]\}$$

and the appropriate phase composition and compressibility factor are used.After that K-value can be calculaed from

$$K_i' = \phi_L'/\phi_{iv} = y_i/x_i'$$

$$K_i'' = \phi_L''/\phi_{iv} = y_i/x_i''$$

and result of calculation show follow:

Table 4.13 Fugacity Coefficients of Mixture

| Phase | $\phi_{iv}$ | $\phi_{iL}'$ | $\phi_{iL}''$ | $K_i'$ | $K_i''$ |
|---|---|---|---|---|---|
| Methane | 1.3082 | 4.1434 | 2.6086 | 3.1672 | 1.9940 |
| Ethane | 0.6128 | 0.5931 | 0.5851 | 0.9678 | 0.9549 |
| n-docosane | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

**4. Calculation Fraction of Feed in Liquid Phases**

The procedure for search the values of $u_1, u_2$ must be performed, the result of this procedure are shown and Newton-Raphson method be used for finding and convergence is declared when $Q_1$, and $Q_{1'}$ are zero or within tolerance.

**5. Calculation Mole Fraction and K-value**

From relations of:

$$F = V+L'+L''$$

$$1 = \beta+u_1+u_2$$

$$\beta = V/F$$

$$\beta = L'/(L'+L'')$$

$$u_1 = L'/F$$

$$u_2 = L''/F$$

compositions in each phase can be calculated from

$$x_1' = z_1/(\alpha K_1'+(1-\alpha)(\beta+(1-\beta)K_1'/K_1''))$$

$$x_1'' = z_1/(\alpha K_1''+(1-\alpha)(\beta K_1''/K_1'+1-\beta))$$

$$y_1 = K_1'x_1' = K_1''x_1''$$

and the result after calculate can be shown below:

**Table 4.14 Mole Fraction and K-values**

| Phase | Vapor | Liquid I | Liquid II | $K_1'$ | $K_1''$ |
|---|---|---|---|---|---|
| Methane | 0.0870 | 0.0275 | 0.0436 | 3.1672 | 1.9940 |
| Ethane | 0.9130 | 0.9434 | 0.9562 | 0.9678 | 0.9546 |
| n-docosane | 0.0000 | 0.0292 | 0.0002 | 0.0000 | 0.0000 |

For Graboski & Daubert and Peng & Robinson two parameters cubic equations of state the procedure of calculation have the way as Soave-Redlich-Kwong equation, then we did not show in this work.