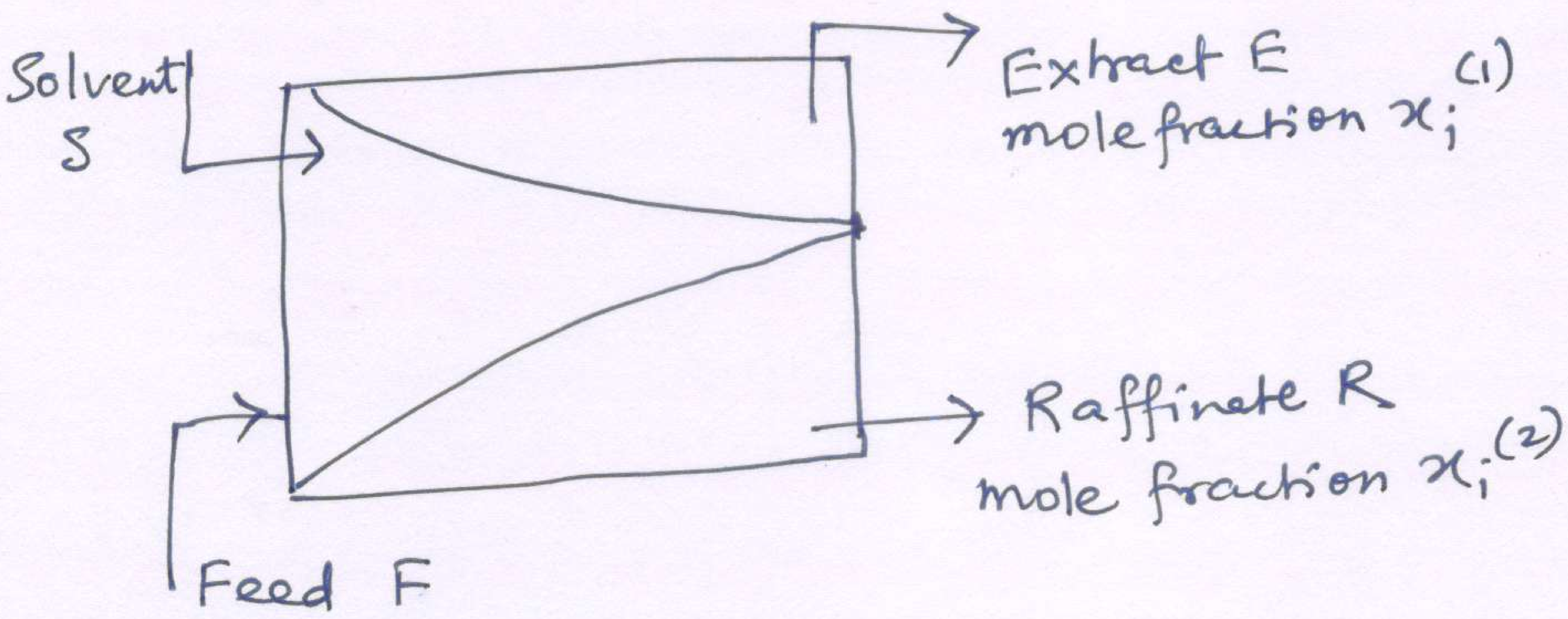
Multicomponent Liquid-Liquid System

Rachford-Rice algorithm (for VLE) is modified as follows.



Distribution Coefficient

$$K_{D_i} = \frac{x_i^{(1)}}{x_i^{(2)}} = K_i$$

$i = 1, 2, \ldots$ No. of components

$$\varphi = \frac{E}{F+S}$$

$0 \le \varphi \le 1$

Overall Mass balance: $E + R = F + S = M$

Component Mass balance: $E x_i^{(1)} + R x_i^{(2)} = M z_i = (F+S) z_i$

Here, z_i is the mole fraction of component i in the mixture (supposed).

Dividing both sides by $(F+S)$ and expressing $x_i^{(1)} = K_i x_i^{(2)}$

$$\frac{E}{F+S} K_i x_i^{(2)} + \frac{R}{F+S} x_i^{(2)} = z_i$$

$$\Rightarrow x_i^{(2)} = \frac{z_i}{\varphi K_i + (1-\varphi)} = \frac{z_i}{1+\varphi(K_i-1)} \quad \ldots\ldots \text{Eq. 1}$$

$$\Rightarrow x_i^{(1)} = \frac{z_i K_i}{1+\varphi(K_i-1)} \quad \ldots\ldots \text{Eq. 2}$$

Solution for φ can be obtained by setting $\sum_{i=1}^{C} x_i^{(1)} - \sum_{i=1}^{C} x_i^{(2)} = 0$

$$\Rightarrow \sum_{i=1}^{C} \frac{z_i(1-K_i)}{1+\varphi(K_i-1)} = 0 = f(\varphi) \quad \ldots\ldots \text{Eq. 3}$$

Equation 3 can be solved by Newton's method with initial guess of φ between 0 and 1.

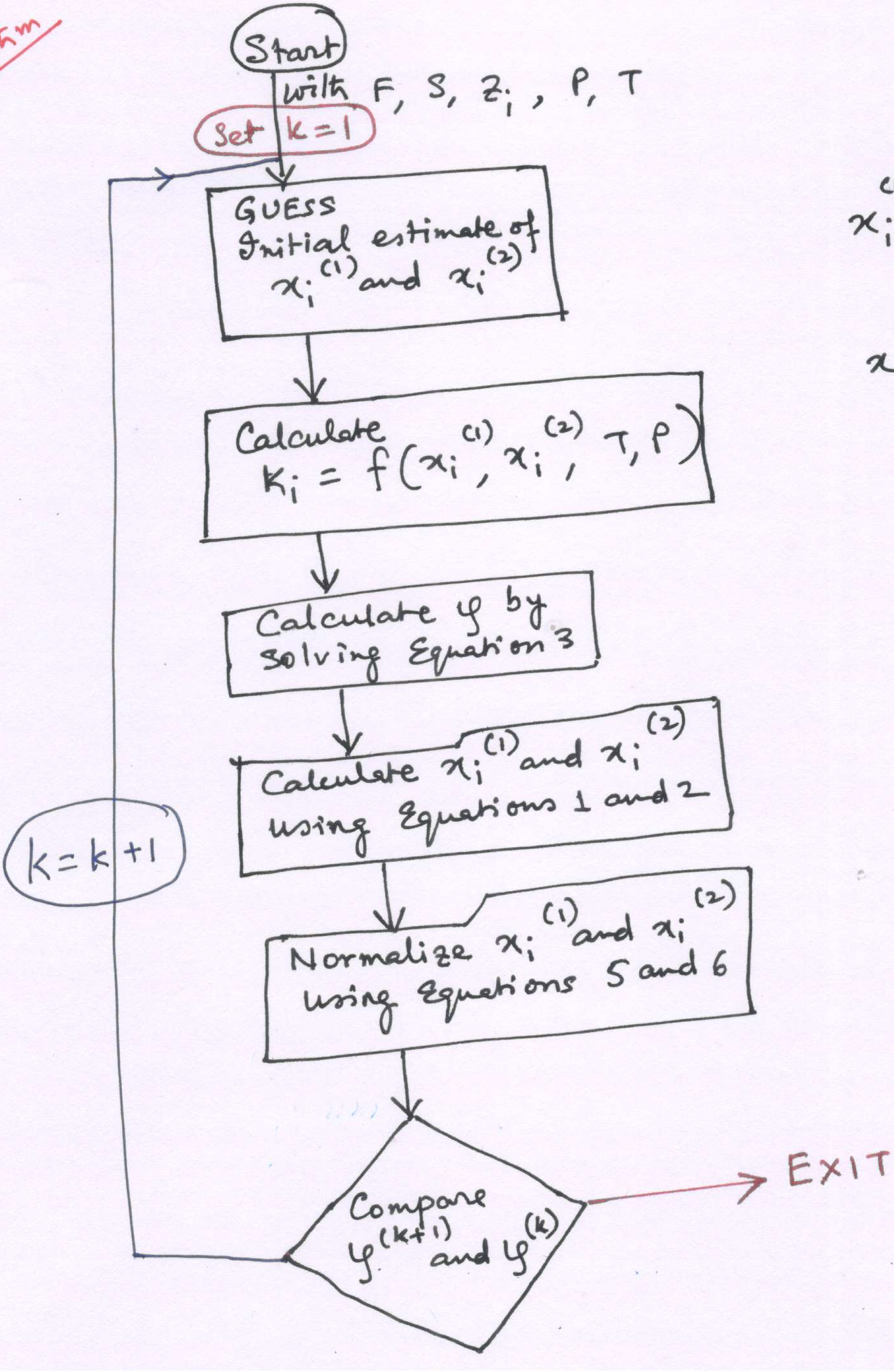
$$\varphi^{(k+1)} = \varphi^{(k)} - \frac{f\left(\varphi^{(k)}\right)}{f'\left(\varphi^{(k)}\right)} \quad \ldots\ldots \text{Eq. 4}$$

where

$$f'(\varphi^{(k)}) = \sum_{i=1}^{C} \frac{z_i(1-K_i)^2}{\left[1+\varphi^{(k)}(K_i-1)\right]^2}$$

Multicomponent Liquid-Liquid system ... contd.

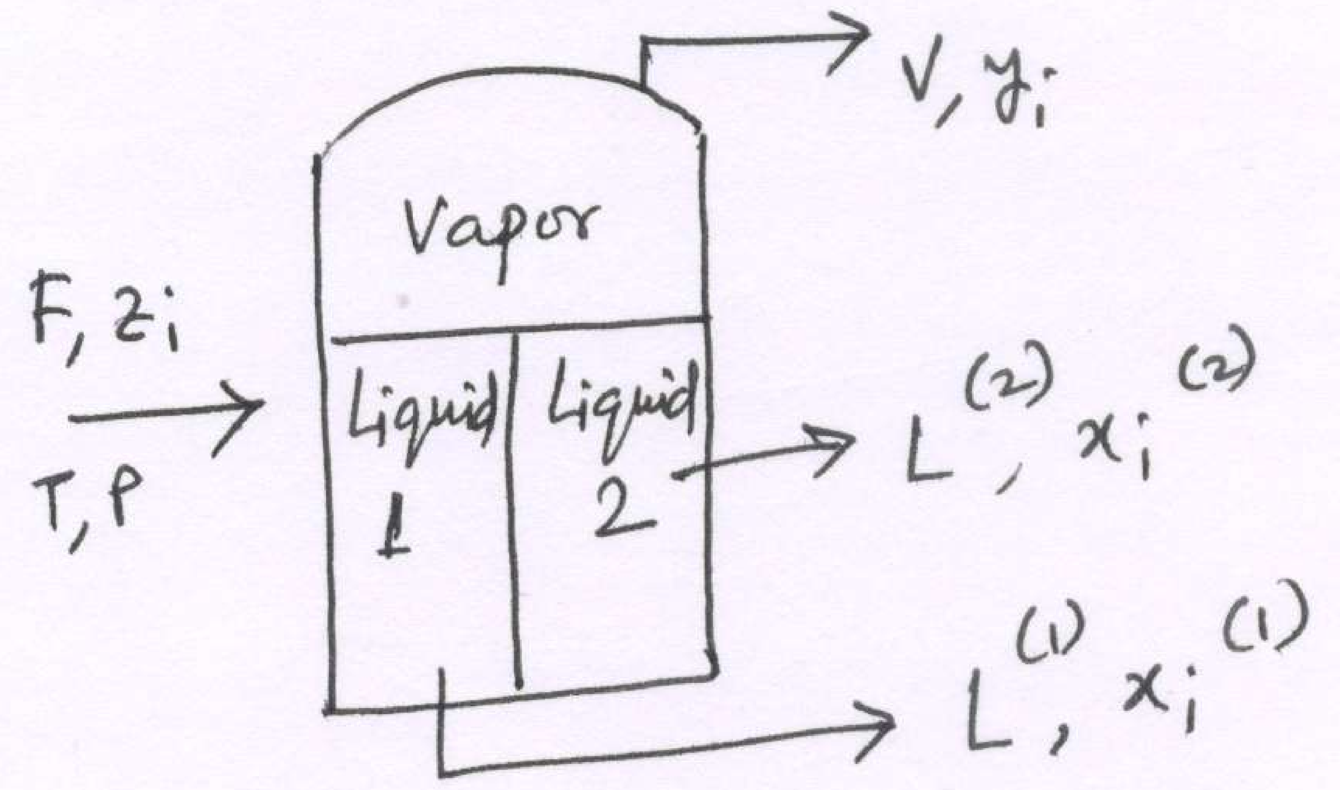
Algorithm



$$x_i^{(1)} = \frac{x_i^{(1)}}{\sum_{j=1}^{c} x_j^{(1)}} \quad \text{... Eq. 5}$$

$$x_i^{(2)} = \frac{x_i^{(2)}}{\sum_{j=1}^{c} x_j^{(2)}} \quad \text{... Eq. 6}$$

Multicomponent Liquid-Liquid-Vapor System



$$F z_i = V y_i + L^{(1)} x_i^{(1)} + L^{(2)} x_i^{(2)} \quad \text{------ Eq. 1}$$

$$\left.\begin{aligned} K_i^{(1)} &= \frac{y_i}{x_i^{(1)}} \\ K_i^{(2)} &= \frac{y_i}{x_i^{(2)}} \end{aligned}\right\} \quad K_{D_i} = \frac{x_i^{(1)}}{x_i^{(2)}} = \frac{K_i^{(2)}}{K_i^{(1)}} \quad \text{------ Eq. 2}$$

Modified Rachford-Rice Procedure

$$\varphi = \frac{V}{F}; \qquad \xi = \frac{L^{(1)}}{L^{(1)} + L^{(2)}}$$

where

$$0 \le \varphi \le 1$$
$$0 \le \xi \le 1$$

$$\Rightarrow \boxed{V = \varphi F} \text{ ----- } \boxed{\begin{aligned} L^{(1)} &= \xi \left[L^{(1)} + L^{(2)}\right] \\ &= \xi (F - V) \\ L^{(2)} &= F - V - L^{(1)} \end{aligned}} \text{ ------ Eq. 3}$$

$$y_i = K_i^{(1)} x_i^{(1)}$$

(After Rearranging Eqn. 1)

$$= K_i^{(1)} \left[\frac{F(z_i) - V y_i - L^{(2)} x_i^{(2)}}{L^{(1)}}\right] \qquad x_i^{(2)} = \frac{y_i}{K_i^{(2)}} \text{ vide Eq. 2}$$

$$= \frac{K_i^{(1)} F z_i}{L^{(1)}} - \frac{K_i^{(1)}}{L^{(1)}} y_i \left[V + \frac{L^{(2)}}{K_i^{(2)}}\right]$$

$$\Rightarrow y_i \left[1 + \frac{K_i^{(1)}}{L^{(1)}} \left\{V + \frac{L^{(2)}}{K_i^{(2)}}\right\}\right] = \frac{K_i^{(1)} F z_i}{L^{(1)}}$$

$$\Rightarrow y_i = \frac{K_i^{(1)} F z_i}{L^{(1)} \left[1 + \frac{K_i^{(1)}}{L^{(1)}} \left\{V + \frac{L^{(2)}}{K_i^{(2)}}\right\}\right]} = \frac{z_i}{\frac{L^{(1)}}{K_i^{(1)} F} \left[1 + \frac{K_i^{(1)}}{L^{(1)}} \left\{V + \frac{L^{(2)}}{K_i^{(2)}}\right\}\right]}$$

$$= \frac{z_i}{\frac{L^{(1)}}{K_i^{(1)} F} + \frac{V}{F} + \frac{L^{(2)}}{K_i^{(2)} F}} = \frac{z_i}{\xi \frac{(1-\varphi)}{K_i^{(1)}} + \frac{(1-\varphi)(1-\xi)}{K_i^{(2)}} + \varphi} \quad \text{---- Eq. 4}$$

From Eq. 3

$$\frac{L^{(1)}}{F} = \frac{\xi (F - V)}{F} = \xi - \xi \frac{V}{F}$$
$$= \xi \left(1 - \frac{V}{F}\right) = \xi (1 - \varphi)$$

$$\frac{L^{(2)}}{F} = \frac{F - V - L^{(1)}}{F} = 1 - \frac{V}{F} - \frac{L^{(1)}}{F}$$
$$= 1 - \varphi - \xi (1 - \varphi)$$
$$= (1 - \varphi)(1 - \xi)$$

Multicomponent Liquid-Liquid-Vapor System ... contd.

from Equation 2 $$x_i^{(1)} = \frac{y_i}{K_i^{(1)}}$$

Using Equation 4

$$x_i^{(1)} = \frac{z_i}{\xi(1-\psi) + (1-\psi)(1-\xi)\frac{K_i^{(1)}}{K_i^{(2)}} + \psi K_i^{(1)}}$$

And $$x_i^{(2)} = \frac{z_i}{\xi(1-\psi)\frac{K_i^{(2)}}{K_i^{(1)}} + (1-\psi)(1-\xi) + \psi K_i^{(2)}}$$

Unlike the liquid-liquid system, the above system of equations ~~have~~ has two unknowns, ψ and ξ. The two equations required to solve for ψ and ξ would be

$$\sum x_i^{(1)} - \sum y_i = 0$$

$$\sum x_i^{(1)} - \sum x_i^{(2)} = 0$$

$$\Rightarrow \sum_{i=1}^{c} \frac{z_i\left(1-K_i^{(1)}\right)}{\xi(1-\psi) + (1-\psi)(1-\xi)\frac{K_i^{(1)}}{K_i^{(2)}} + \psi K_i^{(1)}} = 0$$

and $$\sum_{i=1}^{c} \frac{z_i\left(1-\frac{K_i^{(1)}}{K_i^{(2)}}\right)}{\xi(1-\psi) + (1-\psi)(1-\xi)\frac{K_i^{(1)}}{K_i^{(2)}} + \psi K_i^{(1)}} = 0$$

The two non-linear equations are to be solved simultaneously by Newton's method for two unknowns ψ and ξ

It may not be obvious that three phases will be present.
First search for three phase solution, as above.
If $0 \le \psi \le 1$ and $0 \le \xi \le 1$ are not satisfied, search for $L^{(1)}, L^{(2)}$ solution and $V, L^{(1)}$ solution.
If the bounds are not satisfied $\Rightarrow$ $\boxed{\text{Single phase}}$