CHAPTER IV

CALCULATION PROCEDURES AND CALCULATION WORK

4.1 Determination of Kij

The Kij value in equation 3.8 is determined by back calculation using experimental pressure data of various binary systems reported in the literature.

For convergence method, Fibonacci Optimization Technique is used.

4.2 Determination of Pcal

Pcal is determined by equation fugacity coefficients in the liquid and vapor phases :

$$\hat{f}_i^v = \hat{f}_i^l \tag{4.1}$$

$$\phi_i^v(T, P, y_i)\, y_i = \phi_i^l(T, P, x_i)\, x_i \tag{4.2}$$

Newton - Raphson methods is used as the convergence method to obtain the saturation pressure, Pcal.

4.3 Fibonacci Optimization Technique

The purpose of this technique is to find the minimum of a single variable f(x), non linear function subject to constraints $a \leq x \leq d$. The upper and lower bounds, d and a, are constants. In this work, Fibonacci optimization technique is applied for calculating the binary interaction parameters. The f(x) is the objective function. The a and d are initially guessed binary interaction parameters.

This procedure is an interval elimination search method. Thus, starting with the original boundaries on the independent variable, the interval in which the optimum value of the function occurs is reduced to a final value, the magnitude of which depends on the desired accuracy. The location of points for function evaluations is based on the use of positive integers known as the Fibonacci numbers. No derivatives are required. A specification of the desired accuracy will determine the number of function evaluations. A unimodal function is assumed. Thus the use of multiple starting points is recommended if a multimodal function is suspected. The algorithm proceeds are as follows:

a). Designate the original search interval as L1 with boundaries a1 and b1

b). Predetermine the desired accuracy α and thus the number,N, of required Fibonacci numbers (equals number of required function evaluations)

$$\alpha = \frac{1}{Fn} \quad (4.3)$$

$$F_0 = F_1 = 1 \quad (4.4)$$

$$Fn = Fn\text{-}1 + Fn\text{-}2 \quad ,n \geq 2 \quad (4.5)$$

where is Fn called a Fibonacci number.

c). Place the first two points , X1 and X2 (X1< X2) within L1 at a distance l_1 from each boundary ,

$$l_1 = \frac{Fn\text{-}2}{Fn} L_1 \quad (4.6)$$

$$X1 = a1 + l_1 \quad (4.7)$$

$$X2 = b1 - l_1 \quad (4.8)$$

d). Evaluate the objective function at X1 and X2 . Designate the function as F (X1) and F (X2) . Narrow the search interval as follows:

$$a1 \leq X^* \leq X2 \quad \text{for} \quad F(X1) < F(X2) \quad (4.9)$$

$$X1 \leq X^* \leq b1 \quad \text{for} \quad F(X1) < F(X2) \quad (4.10)$$

where X* is the location of the optimum. The new search interval is given by

$$L_2 = \frac{Fn-1}{Fn} . L1 = L1 - l_1 \qquad (4.11)$$

with boundaries a2 and b2.

e). Place the third point in the new L2 subinterval, symmetric about the remaining point,

$$l_2 = \frac{Fn-3}{Fn-1} L_2 \qquad (4.12)$$

$$X3 = a2 + l_2 \quad \text{or} \quad b2 - l_2 \qquad (4.13)$$

f). Evaluate the objective function F(X3), compare with the function for the remaining in the interval and reduce the interval to

$$L_3 = \frac{Fn-2}{Fn} . L1 = L2 - l_2 \qquad (4.14)$$

h). The process is continued per the preceeding rules for N evaluations.

The general equations are

$$l_k = \frac{F_{N-(k+1)}}{F_{N-(k-1)}} . L_k \qquad (4.15)$$

$$X_{k+1} = a_k + l_k \text{ or } b_k - l_k \quad \text{(symmetric about mid point)}$$

$$L_k = \frac{F_{N-(k-1)}}{F_N} . L_1 = L_{k-1} - l_{k-1} \qquad (4.16)$$

After N-1 evaluations and discarding the appropriate interval at each step, the remaining point will be precisely in the center of the remaining interval. Thus point N is also at the midpoint and is replaced by a point perturbed some small distance ε to one side or the other of the midpoint. The objective function is located is thus determined. A flow sheet illustrating the procedure is given in Figure 4.1

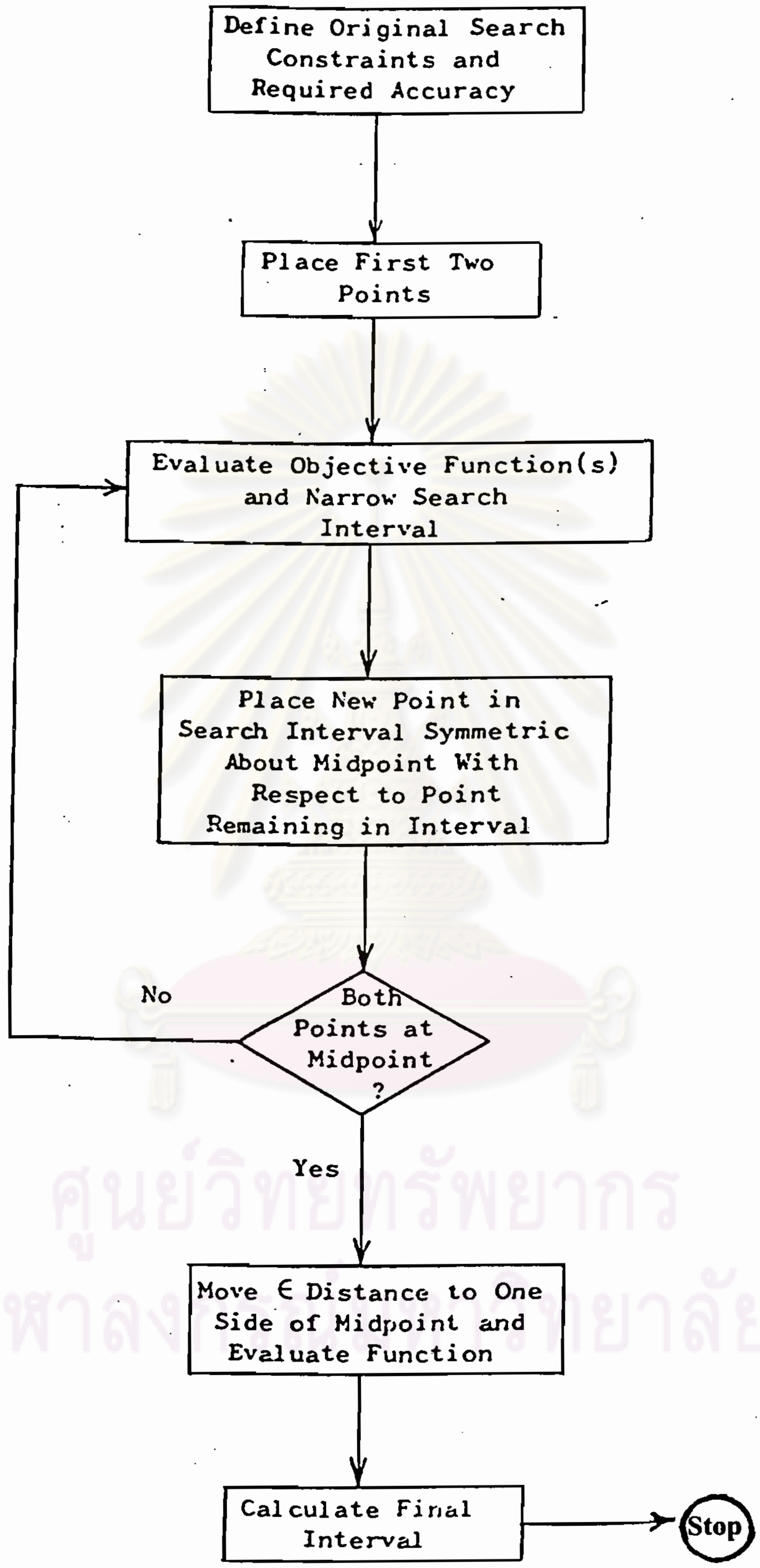

Figure 4.1 Fibonacci (FIBON ALGORITHM) Logic Diagram

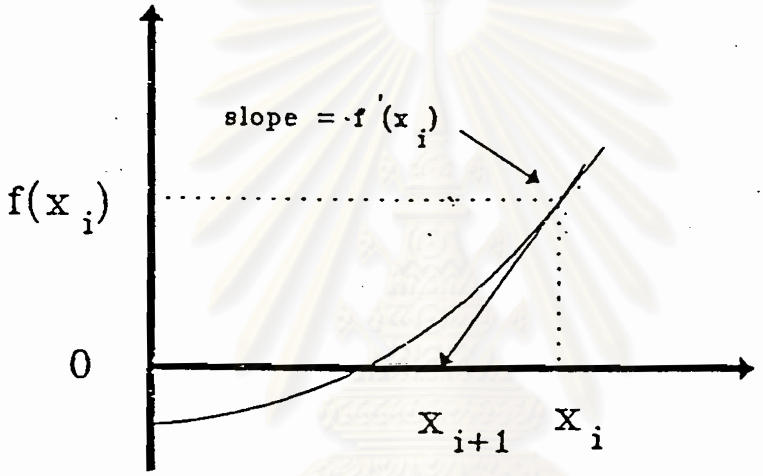

Figure 4.2 Graphical depiction of the Newton - Raphson method

4.4 The Newton-Raphson Method

When only roots are required, which is always the case with equations of state, the Newton-Raphson method is convenient. Figure 4.2 depicts the graphical Newton-Raphson method. If the initial guess at root is Xi ,a tangent can be extended from the point

[Xi , f(Xi)]. The point where this tangent crosses the X axis , Xi+1 usually represents an improved estimate of the root. The Newton-Raphson method can be derived on the basis of this geometrical interpretation. As in Figure 4.2 , the first derivation at Xi is equivalent to the slope:

$$X i = \frac{f(Xi) - 0}{Xi - Xi+1} \qquad (4.17)$$

which can be rearrangeed to yield

$$Xi+1 = Xi - \frac{f(Xi)}{f'(Xi)} \qquad (4.18)$$

which is called the Newton-Raphson formula.

It is applied to quartic equations of state calculation in this work for 2 cases,

Case I : Calculate the roots of quartic equation of state

Case II : To obtain the Saturation pressure ,Pcal

Case I : Calculate the roots of quartic equation of state

From Eq 2. 5 , the equation of state is written as a quartic:

$$V^4+q_3V^3+q_2V^2+q_1V+q_0 = 0 \qquad (4.19)$$

where q_0,q_1,q_2,q_3 are expressed in equation 2.6 - 2.9 respectively. We can write the equation in form of compressibility factor (Z) by the substitutions PV = ZRT or V = ZRT/P,then we obtain.

$$\frac{(ZRT)^4}{P^4} + q_3\frac{(ZRT)^3}{P^3} + q_2\frac{(ZRT)^2}{P^2} + q_1\frac{(ZRT)}{P} + q_0 = 0 \qquad (4.20)$$

devided by $(RT/P)^4$,which give

$$Z^4 + \frac{q_3Z^3}{(RT/P)} + \frac{q_2Z^2}{(RT/P)^2} + \frac{q_1Z}{(RT/P)^3} + \frac{q_0}{(RT/P)^4} = 0 \qquad (4.21)$$

let $Q1 = \dfrac{q_3}{(RT/P)}$ (4.22)

$Q2 = \dfrac{q_2}{(RT/P)^2}$ (4.23)

$Q3 = \dfrac{q_1}{(RT/P)^3}$ (4.24)

$Q4 = \dfrac{q_0}{(RT/P)^4}$ (4.25)

So Eq 4.21 becomes

$$Z^4 + Q1\,Z^3 + Q2\,Z^2 + Q3Z + Q4 = 0 \qquad (4.26)$$

And, Eqs (4.22)-(4.25) become ,on rearrangement,

$$Q1 = \frac{P}{RT}[-2K_0\beta + e] - 1 \qquad (4.27)$$

$$Q2 = \frac{P}{RT}(\beta k_0 - \beta k_1 - e) + \frac{P^2}{(RT)^2}[k_0^2\beta^2 - 2\beta k_0 e] + \frac{a\,P}{(RT)^2} \qquad (4.28)$$

$$Q3 = \frac{1}{(RT)^3}[P^3 e\, k_0^2\beta^2 + P^2\beta k_0 c - P^2\beta\, k_0\, a] + \frac{1}{(RT)^2}[P^2 e\beta k_0 - P^2 e\,\beta\, k_1] \qquad (4.29)$$

$$Q4 = \frac{-P^3 c\, k_0^2\beta^2}{(RT)^4} \qquad (4.30)$$

for the purpose to use the Newton-Raphson formula to calculate the roots of quartic equation of state

$$f(Zi) = Z^4 + Q1Z^3 + Q2\,Z^2 + Q3\,Z + Q4 \qquad (4.31)$$

$$f(Zi) = 4Z^3 + 3\,Q1Z^2 + 2\,Q2\,Z + Q3 \qquad (4.32)$$

$$Z_{i+1} = Z_i + \frac{f(Zi)}{f'(Zi)} \qquad (4.33)$$

while the quartic equation yields four roots , one root is always negative and hence physically meaningless , and three roots behave like three roots of a cubic equation. For the case with vapour liquid equilibrium calculation in binary systems we define Zv is the compressibility factor in vapour phase and Zl is the compressibility factor in liquid phase. Where the value of Zv,Zl are nearly 1 and 0.1 consequently.

Case II: To obtain the Saturation pressure ,Pcal

For the purpose to calculate the pressure of the system from Quartic EOS, the initial pressure must be guessed at the first step of calculation . This suitable method leads to find the answer fast and correctly. So we obtain the following expressions

$$P_{i+1} = P_i - \frac{f(Zi)}{f'(Zi)} \qquad (4.34)$$

for binary mixture

$$P_i = (x_1P_1sat + x_2P_2sat)/2 \qquad (4.35)$$

$$f(P_i) = x_1\hat{\phi}1^{l} - y_1\hat{\phi}1^{v} \qquad (4.36)$$

$$f(P_i) = x_1\frac{\partial(\hat{\phi}1^{l})}{\partial P} - y_1\frac{\partial(\hat{\phi}1^{v})}{\partial P} \qquad (4.37)$$

and absolute value of $|x_1\hat{\phi}1^{l} - y_1\hat{\phi}1^{v}|$ approaches 0.0001

4.5 Derivation of fugacity coefficient equation

4.5.1 General formula

General formula of partial molar properties requires differentiation with respect to composition, and we assume the availability of corresponding-states correlation for property M ,of the form

$$M = \mu(Tpr, Ppr, \pi p)$$

when $Tpr = T/Tpc$ (4.38)

$Ppr = P/Ppc$ (4.39)

$\pi p = \sum Xi\,\pi i$ (4.40)

where Tpr = pseudo reduce temperature

Ppr = pseudo reduce pressure

and μ is the same function developed for the correlation of M for pur fluids. By definition

$$\bar{M}i = \left[\frac{\partial(n\,M)}{\partial ni}\right]_{T,P,nj} \qquad (4.41)$$

and thus

$$\overline{M}_i = M + n\left[\frac{\partial M}{\partial n_i}\right]_{T,P,n_j} \tag{4.42}$$

For practical calculation, the most important partial molar properties is $\ln\hat{\phi}_i$.

and the fugacity coefficient of pure i is $\ln\hat{\phi}$

$$\ln\phi = 1/RT \int_{\infty}^{V_t}\left[\frac{RT}{V_t} - \left(\frac{\partial P}{\partial n_i}\right)_{t,V_t,n_j}\right] dV_t - \ln z \tag{4.43}$$

Since

$$\overline{M}_i = \ln\hat{\phi}_i \tag{4.44}$$

$$M = \ln\phi \tag{4.45}$$

Sustitution of the last two expressions into Eq 4.42 gives

$$\ln\hat{\phi}_i = \ln\phi + n\left[\frac{\partial \ln\phi}{\partial n_i}\right]_{T,P,n_j} \tag{4.46}$$

4.5.2 $\hat{\phi}_i$ based on Quartic EOS

$$P = \frac{RT}{(V - k_0\beta)} + \frac{\beta k_1 RT}{(V - k_0\beta)^2} - \frac{aV + k_0\beta c}{V(V+e)(V - k_0\beta)} \tag{4.47}$$

$$\ln\frac{f}{P} = Z - 1 - \ln Z + \frac{1}{RT}\int_{\infty}^{V}\left(\frac{RT}{V} - P\right) dV \tag{4.48}$$

by Eq 4.47 ,

$$\frac{RT}{V} - P = \frac{RT}{V} - \frac{RT}{(V - k_0\beta)} + \frac{\beta k_1 RT}{(V - k_0\beta)^2} - \frac{aV + k_0\beta c}{V(V+e)(V - k_0\beta)} \tag{4.49}$$

$$\int_{\infty}^{V} \left(\frac{RT}{V} - P \right) dV = \int_{\infty}^{V} \left[\frac{RT}{V} - \frac{RT}{(V - k_0\beta)} + \frac{\beta k_1 RT}{(V - k_0\beta)^2} - \frac{aV + k_0\beta c}{V(V+e)(V - k_0\beta)} \right] dV \quad (4.50)$$

$$\int_{\infty}^{V} \frac{RT}{V} dV = RT \ln V \quad (4.51)$$

$$\int_{\infty}^{V} \frac{RT}{(V - k_0\beta)} dV = RT \ln (V - k_0\beta) \quad (4.52)$$

$$\int_{\infty}^{V} \frac{\beta k_1 RT}{(V - k_0\beta)^2} dV = \beta k_1 RT \int_{\infty}^{V} \frac{1}{(V - k_0\beta)^2} dV \quad (4.53)$$

$$= \frac{-\beta k_1 RT}{(V - k_0\beta)} \quad (4.54)$$

$$\int_{\infty}^{V} \frac{a}{(V+e)(V - k_0\beta)} dV = a \int_{\infty}^{V} \frac{1}{(V+e)(V - k_0\beta)} dV \quad (4.55)$$

Integrate by fraction

Assume $G = k_0\beta$ **; constant**

$$\frac{1}{(V+e)(V-G)} = \frac{A}{(V+e)} + \frac{B}{(V-G)} \quad (4.56)$$

$$AV - AG - BV + Be = 1 \quad (4.57)$$

$$(A+B)V - AG + Be = 1 \quad (4.58)$$

$$A+B = 0 \; , \; A = -B \quad (4.59)$$

$$Be - AG = -1 \quad (4.60)$$

$$B = 1 / (G+e) \quad (4.61)$$

$$A = -1 / (G+e) \quad (4.62)$$

$$\int_{\infty}^{V} \frac{a}{(V+e)(V-k_0\beta)}\, dV = a \int_{\infty}^{V} \frac{-1}{(V+e)(G+e)}\, dV + a \int_{\infty}^{V} \frac{1}{(V-G)(G+e)}\, dV \qquad (4.63)$$

$$= a\left[\frac{-\ln (V+e)}{(G+e)} + \frac{\ln (V-G)}{(G+e)}\right] \qquad (4.64)$$

$$= \frac{a}{(k_0\beta+e)} \cdot \ln \frac{(V-k_0\beta)}{(V+e)} \qquad (4.65)$$

$$\int_{\infty}^{V} \frac{k_0\beta c}{V(V+e)(V-k_0\beta)}\, dV = k_0\beta c \int_{\infty}^{V} \frac{1}{V(V+e)(V-k_0\beta)}\, dV \qquad (4.66)$$

$$\int_{\infty}^{V} \frac{k_0\beta c}{V(V+e)(V-k_0\beta)}\, dV = Gc \int_{\infty}^{V} \frac{1}{V(V+e)(V-k_0\beta)}\, dV \qquad (4.67)$$

$$\frac{1}{V(V+e)(V-k_0\beta)} = \frac{A}{V} + \frac{B}{(V+e)} + \frac{C}{(V-G)} \qquad (4.68)$$

$$A(V+e)(V-G) + BV(V-G) + CV(V+e) = 1 \qquad (4.69)$$

$$A(V^2-GV+eV-Ge) + BV^2 - BGV + CV^2 + CVe = 1 \qquad (4.70)$$

$$(A+B+C)V^2 = 0 \qquad (4.71)$$

$$(-AG + Ae - BG + Ce)V = 0 \qquad (4.72)$$

$$-AGe = 1 \qquad (4.73)$$

So $A = -1/Ge$, $B = 1/e(G+e)$, $C = 1/(G^2+Ge)$ (4.74)

Then

$$GC\int_{\infty}^{V} \frac{1}{V(V+e)(V-k_0\beta)}\, dV = GC\int_{\infty}^{V} \frac{-1}{GVe}\, dV + \int_{\infty}^{V} \frac{1}{e(G+e)(V+e)}\, dV + \int_{\infty}^{V} \frac{1}{(G^2+Ge)(V-G)}\, dV$$

$$= GC\left[\frac{-\ln V}{Ge} + \frac{\ln (V+e)}{e(G+e)} + \frac{\ln (V-G)}{(G^2+Ge)}\right] \qquad (4.75)$$

$$= k_0\beta c\left[\frac{\ln (V-k_0\beta)}{(k_0\beta)^2+(k_0\beta e)} + \frac{\ln (V+e)}{(e^2+k_0\beta e)} - \frac{\ln V}{k_0\beta e}\right] \qquad (4.76)$$

$$\int_{\infty}^{V} \frac{k_0 \beta c}{V(V+e)(V-k_0\beta)}\, dV = k_0\beta c\left[\frac{\ln (V-k_0\beta)}{(k_0\beta)^2+(k_0\beta e)} + \frac{\ln (V+e)}{(e^2+k_0\beta e)} - \frac{\ln V}{k_0\beta e}\right] \tag{4.77}$$

We have

$$\int_{\infty}^{V} \left(\frac{RT}{V} - P\right) dV = RT \ln V - RT \ln (V-k_0\beta) + \frac{\beta k_1 RT}{(V-k_0\beta)} + \frac{a}{(k_0\beta+e)}\left[\ln \frac{(V-k_0\beta)}{(V+e)}\right]$$
$$+ k_0\beta c\left[\frac{\ln (V-k_0\beta)}{(k_0\beta)^2+(k_0\beta e)} + \frac{\ln (V+e)}{(e^2+k_0\beta e)} - \frac{\ln V}{k_0\beta e}\right] \tag{4.78}$$

$$\ln \phi = Z-1-\ln Z + \frac{1}{RT}\int_{\infty}^{V}\left(\frac{RT}{V} - P\right) dV \tag{4.79}$$

so

$$\ln \phi = Z-1-\ln Z + \ln\frac{V}{(V-k_0\beta)} + \frac{\beta k_1}{(V-k_0\beta)} + \frac{a}{RT(k_0\beta+e)}\ln\left[\frac{(V-k_0\beta)}{V+e)}\right]$$
$$+\frac{k_0\beta c}{RT}\left[\frac{\ln (V-k_0\beta)}{(k_0\beta)^2+(k_0\beta e)} + \frac{\ln (V+e)}{(e^2+k_0\beta e)} - \frac{\ln V}{k_0\beta e}\right] \tag{4.80}$$

Since $\quad \bar{M}_i = M + n\left(\frac{\partial M}{\partial n_i}\right)_{T,P,n_j}$ (4.81)

By $\quad M = \ln \phi$ gives (4.82)

$$\ln \hat{\phi}_i = \ln \phi + n\left(\frac{\partial \ln \phi}{\partial n_i}\right)_{T,P,n_j} \tag{4.83}$$

$$\left(\frac{\partial \ln \phi}{\partial n_i}\right)_{T,P,n_j} = \left(\frac{\partial \ln \phi}{\partial \beta}\right)_{a,e,c}\left(\frac{\partial \beta}{\partial n_i}\right)_{n_j} + \left(\frac{\partial \ln \phi}{\partial c}\right)_{a,e,\beta}\left(\frac{\partial c}{\partial n_i}\right)_{n_j} + \left(\frac{\partial \ln \phi}{\partial a}\right)_{c,e,\beta}\left(\frac{\partial a}{\partial n_i}\right)_{n_j}$$
$$+ \left(\frac{\partial \ln \phi}{\partial e}\right)_{a,c,\beta}\left(\frac{\partial e}{\partial n_i}\right)_{n_j} \tag{4.84}$$

so we require the value $\left(\frac{\partial \ln \phi}{\partial \beta}\right)_{a,e,c}$, $\left(\frac{\partial \ln \phi}{\partial c}\right)_{a,e,\beta}$, $\left(\frac{\partial \ln \phi}{\partial a}\right)_{c,e,\beta}$, $\left(\frac{\partial \ln \phi}{\partial e}\right)_{a,c,\beta}$

$$\frac{(\partial \ln \phi)_{a,e,c}}{(\partial \beta)} = \frac{\partial}{(\partial \beta)}\left[Z - 1 - \ln Z + \ln \frac{V}{(V - k_0\beta)} + \frac{\beta k_1}{(V - k_0\beta)} + \frac{a}{RT(k_0\beta + e)} \ln \frac{(V - k_0\beta)}{(V+e)}\right]$$

$$+ \frac{\partial}{(\partial \beta)}\left(\frac{k_0\beta c}{RT}\left[\frac{\ln (V - k_0\beta)}{(k_0\beta)^2 + (k_0\beta e)} + \frac{\ln (V+e)}{(e^2 + k_0\beta e)} - \frac{\ln V}{k_0\beta e}\right]\right) \quad (4.85)$$

$$\frac{(\partial \ln \phi)_{a,e,c}}{(\partial \beta)} = \frac{(\partial Z)_{a,e,c}}{(\partial \beta)} \quad \frac{(\partial\ 1)_{a,e,c}}{(\partial \beta)} \quad \frac{(\partial\ \ln Z)_{a,e,c}}{(\partial \beta)} \quad \frac{(\partial\ (\ln V/(V - k_0\beta)))_{a,e,c}}{(\partial \beta)}$$

$$+ \frac{\partial(\beta k_1/(V - k_0\beta))_{a,e,c}}{(\partial \beta)} + \frac{\partial}{(\partial \beta)}\left[\frac{a}{RT(k_0\beta + e)} \ln \frac{(V - k_0\beta)}{(V+e)}\right]$$

$$+ \frac{\partial}{(\partial \beta)}\left(\frac{\beta k_0 c}{RT}\left[\frac{\ln (V - k_0\beta)}{(k_0\beta)^2 + (k_0\beta e)} + \frac{\ln (V+e)}{(e^2 + k_0\beta e)} - \frac{\ln V}{k_0\beta e}\right]\right) \quad (4.86)$$

find $\frac{(\partial z)_{a,e,c}}{\partial \beta}$

$$Z = \left(\frac{RT}{(V - k_0\beta)} + \frac{\beta k_1 RT}{(V - k_0\beta)^2} - \frac{aV + k_0\beta c}{V(V+e)\ (V - k_0\beta)}\right) \cdot \frac{V}{RT}$$

$$Z = \frac{V}{(V - k_0\beta)} + \frac{\beta k_1}{(V - k_0\beta)^2} - \frac{aV + k_0\beta c}{(V+e)\ (V - k_0\beta)RT}$$

$$Z = \frac{V}{(V - k_0\beta)}\left(1 + \frac{\beta k_1}{(V - k_0\beta)} - \frac{a}{(V+e)RT} - \frac{k_0\beta c}{(V+e)RT}\right)$$

$$\frac{(\partial z)_{a,e,c}}{\partial \beta} = \frac{V}{(V - k_0\beta)}\left(\frac{(V - k_0\beta)k_1 + k_0 k_1 \beta}{(V - k_0\beta)^2} - \frac{k_0 c}{V(V+e)RT}\right)$$

$$+ \frac{V}{(V - k_0\beta)^2}\left(1 + \frac{\beta k_1}{(V - k_0\beta)} - \frac{a}{(V+e)RT} - \frac{k_0\beta c}{V(V+e)RT}\right)$$

$$\frac{(\partial z)_{a,e,c}}{\partial\beta} = \frac{V}{(V - k_0\beta)} \cdot \left(\frac{k_1}{(V - k_0\beta)} + \frac{k_0 k_1 \beta}{(V - k_0\beta)^2} - \frac{k_0 c}{V(V+e)RT} \right.$$

$$\left. + \frac{k_0}{(V - k_0\beta)} + \frac{k_0 k_1 \beta}{(V - k_0\beta)^2} - \frac{ak_0 V + k_0^2\beta c}{V(V - k_0\beta)(V+e)RT} \right)$$

$$\frac{(\partial z)_{a,e,c}}{\partial\beta} = \frac{V}{(V - k_0\beta)} \cdot \left(\frac{k_0 + k_1}{(V - k_0\beta)} + \frac{2k_0 k_1 \beta}{(V - k_0\beta)^2} \right)$$

$$- \frac{V}{(V - k_0\beta)RT} \cdot \left(\frac{k_0 c}{V(V+e)} + \frac{a\ k_0}{(V+e)(V - k_0\beta)} + \frac{k_0^2\beta c}{V(V+e)(V - k_0\beta)} \right) \quad (4.87)$$

$$P = \frac{RT}{(V - k_0\beta)} + \frac{\beta k_1 RT}{(V - k_0\beta)^2} - \frac{aV + k_0\beta c}{V(V+e)(V - k_0\beta)}$$

find $\frac{(\partial z)_{a,e,c}}{\partial\beta}$

from $Z = PV/RT$ so

$$\ln Z = \ln\left(P \cdot \frac{V}{RT}\right) = \ln P + \ln\frac{V}{RT} \quad (4.88)$$

and
$$\frac{(\partial \ln z)_{a,e,c}}{\partial\beta} = \frac{(\partial \ln P)_{a,e,c}}{\partial\beta} + \frac{(\partial \ln V/RT)_{a,e,c}}{\partial\beta} \quad (4.89)$$

$$\frac{(\partial \ln V/RT)_{a,e,c}}{\partial\beta} = 0 \quad (4.90)$$

$$\frac{(\partial \ln z)_{a,e,c}}{\partial\beta} = \frac{1}{P} \cdot \frac{(\partial P)_{a,e,c}}{\partial\beta} \tag{4.91}$$

$$\frac{(\partial P)_{a,e,c}}{\partial\beta} = \frac{RT\,k_0}{(V - k_0\beta)^2} + \frac{k_1 (V - k_0\beta)^2 RT - 2\beta k_1 RT (V - k_0\beta)(-k_0)}{(V - k_0\beta)^4}$$

$$- \frac{(V(V+e)(V - k_0\beta)(k_0 c) - (aV + k_0\beta c)V(V+e)(-k_0))}{V^2 (V - k_0\beta)^2 (V+e)^2}$$

$$= \frac{RT\,k_0}{(V - k_0\beta)^2} + \frac{k_1 RT}{(V - k_0\beta)^2} + \frac{2k_0 k_1 RT\beta}{(V - k_0\beta)^3} - \frac{k_0 c}{V(V - k_0\beta)(V+e)}$$

$$- \frac{k_0 (aV + k_0\beta c)}{V(V - k_0\beta)^2(V+e)} \tag{4.92}$$

find

$$\frac{(\partial \ln z)_{a,e,c}}{\partial\beta} = \frac{1}{P} \cdot \frac{(\partial P)_{a,e,c}}{\partial\beta} = \frac{1}{P}\left(\frac{RT\,k_0}{(V - k_0\beta)^2} + \frac{k_1 RT}{(V - k_0\beta)^2} \right.$$

$$\left. + \frac{2k_0 k_1 RT\beta}{(V - k_0\beta)^3} - \frac{k_0 c}{V(V - k_0\beta)(V+e)} - \frac{k_0 (aV + k_0\beta c)}{V(V - k_0\beta)^2(V+e)} \right) \tag{4.93}$$

$$\frac{(\partial(\ln V / (V - k_0\beta)))_{a,e,c}}{\partial\beta} = \frac{k_0}{(V - k_0\beta)} \tag{4.94}$$

$$\frac{(\partial(k_1\beta / (V - k_0\beta)))_{a,e,c}}{\partial\beta} = \frac{(V - k_0\beta)k_1 - k_1\beta(-k_0)}{(V - k_0\beta)^2} \tag{4.95}$$

$$= \frac{a\ .\ (V+e)(V+e)(-k_0)}{RT\,(k_0\beta + e)\,(V - k_0\beta)(V+e)^2} + \frac{\ln(V - k_0\beta)\,(-a\,RT\,k_0)}{(V+e)R^2T^2\,(k_0\beta + e)^2}$$

$$= \frac{-a.\ k_0}{RT\,(k_0\beta + e)} \cdot \left(\frac{1}{(V - k_0\beta)} + \frac{\ln(V - k_0\beta)/(V+e)}{(k_0\beta + e)} \right) \qquad (4.96)$$

$$\frac{\partial}{\partial\beta}\left[\frac{k_0\beta c\ .}{RT} \left[\frac{\ln(V - k_0\beta)}{(k_0\beta)^2 + (k_0\beta e)} + \frac{\ln(V+e)}{e^2 + k_0\beta e} - \frac{\ln\ V}{k_0\beta e} \right] \right]_{a,e,c}$$

$$= \frac{k_0 c}{RT} \left(\frac{\ln(V - k_0\beta)}{(k_0\beta)^2 + (k_0\beta e)} + \frac{\ln(V+e)}{e^2 + k_0\beta e} - \frac{\ln\ V}{k_0\beta e} \right)$$

$$+ \frac{k_0 c}{RT} \left(\frac{\frac{((k_0\beta)^2 + k_0\beta e)(-k_0)}{(V - k_0\beta)} - \ln(V - k_0\beta).(2k_0^{\,2}\beta + k_0 e)}{((k_0\beta)^2 + k_0\beta e)^2} \right)$$

$$- \frac{k_0 e.\ln(V+e)}{(e^2 + k_0\beta e)} + \frac{k_0 e.\ \ln V}{(k_0\beta e)^2} \Bigg) \qquad (4.97)$$

$$= \frac{k_0 c}{RT} \left(\frac{\ln(V - k_0\beta)}{(k_0\beta)^2 + k_0\beta e} + \frac{\ln\ (V+e)}{(e^2 + k_0\beta e)} - \frac{\ln\ V}{k_0\beta e} \right)$$

$$+ \left(\frac{k_0^{\,2}\beta c e}{RT} \left(\frac{\ln V}{(k_0\beta e)^2} - \frac{1}{(V - k_0\beta)((k_0\beta)^2 + k_0\beta e)} - \frac{\ln(V+e)}{(e^2 + k_0\beta e)} \right) \right.$$

$$- \frac{k_0 \beta c (\ln (V - k_0 \beta))(2k_0^2\beta + k_0 e))}{RT \quad ((k_0 \beta)^2 + k_0 \beta e)^2} \qquad (4.98)$$

$$\frac{(\partial \ln \varnothing)_{a,e,c}}{\partial \beta} = \frac{V}{(V - k_0 \beta)} \left(\frac{k_0 + k_1}{(V - k_0 \beta)} + \frac{2 \beta k_0 k_1}{(V - k_0 \beta)^2} \right)$$

$$- \frac{V}{(V - k_0 \beta) RT} \left(\frac{k_0 c}{V(V+e)} + \frac{a k_0}{(V+e)(V - k_0 \beta)} + \frac{k_0^2 \beta c}{V(V+e)(V - k_0 \beta)} \right)$$

$$- \frac{1}{P} \left(\frac{RT(k_0 + k_1)}{(V - k_0 \beta)^2} + \frac{2 \beta k_0 k_1 RT}{(V - k_0 \beta)^3} - \frac{k_0 c}{V(V+e)(V - k_0 \beta)} - \frac{k_0 (aV + k_0 \beta c))}{V(V+e)(V - k_0 \beta)} \right.$$

$$+ \frac{k_0}{(V - k_0 \beta)} + \left(\frac{k_1}{(V - k_0 \beta)} + \frac{\beta k_0 k_1}{(V - k_0 \beta)^2} \right)$$

$$+ \frac{(-a k_0)}{RT (k_0 \beta + e)} \cdot \left(\frac{1}{(V - k_0 \beta)} + \frac{\ln((V - k_0 \beta)/(V+e))}{(k_0 \beta + e)} \right)$$

$$+ \frac{k_0 c}{RT} \left(\frac{\ln(V - k_0 \beta)}{(k_0 \beta)^2 + k_0 \beta e} + \frac{\ln(V+e)}{(e^2 + k_0 \beta e)} - \frac{\ln V}{k_0 \beta e} \right)$$

$$+ \frac{k_0^2 \beta e c}{RT} \left(\frac{\ln V}{(k_0 \beta e)^2} - \frac{1}{(V - k_0 \beta)((k_0 \beta)^2 + k_0 \beta e)} - \frac{\ln(V+e)}{(e^2 + k_0 \beta e)^2} \right)$$

$$- \frac{k_0 \beta e \cdot (\ln(V - k_0 \beta)) \cdot (2k_0^2 \beta + k_0 e)}{RT \quad ((k_0 \beta)^2 + k_0 \beta e)^2}$$

$$\frac{(\partial \ln \varnothing)_{a,e,\beta}}{\partial c} = \frac{(\partial Z)_{a,e,\beta}}{\partial c} - \frac{(\partial \ln Z)_{a,e,\beta}}{\partial c} \quad (4.99)$$

$$+ \frac{(\partial}{\partial c}\left(\frac{k_0 \beta c}{RT}\left(\frac{\ln(V - k_0\beta)}{((k_0\beta)^2 + k_0\beta e)} + \frac{\ln(V+e)}{(e^2 + k_0\beta e)} - \frac{\ln V}{k_0\beta e}\right)\right)_{a,e,c} \quad (4.100)$$

and $$\frac{(\partial Z)_{a,e,\beta}}{\partial c} = \frac{-k_0\beta}{RT\,(V+e)(V-k_0\beta)} \quad (4.101)$$

$$\frac{(\partial \ln Z)_{a,e,\beta}}{\partial c} = \frac{1}{P}\cdot\frac{(\partial P)_{a,e,\beta}}{\partial c} = \frac{-k_0\beta}{PV(V+e)(V-k_0\beta)} \quad (4.102)$$

$$\frac{(\partial}{\partial c}\left(\frac{k_0\beta c}{RT}\cdot\left(\frac{\ln(V-k_0\beta)}{((k_0\beta)^2 + k_0\beta e)} + \frac{\ln(V+e)}{(e^2 + k_0\beta e)} - \frac{\ln V}{k_0\beta e}\right)\right)_{a,e,\beta}$$

$$= \frac{k_0\beta}{RT}\left(\frac{\ln(V-k_0\beta)}{((k_0\beta)^2 + k_0\beta e)} + \frac{\ln(V+e)}{(e^2 + k_0\beta e)} - \frac{\ln V}{k_0\beta e}\right) \quad (4.103)$$

Then $$\frac{(\partial \ln \varnothing)_{a,e,\beta}}{\partial c} = \frac{k_0\beta\,(1/PV - 1/RT)}{(V+e)(V-k_0\beta)}$$

$$+ \frac{k_0\beta}{RT}\left(\frac{\ln(V-k_0\beta)}{((k_0\beta)^2 + k_0\beta e)} + \frac{\ln(V+e)}{(e^2 + k_0\beta e)} - \frac{\ln V}{k_0\beta e}\right) \quad (4.104)$$

$$\frac{(\partial \ln \varnothing)_{c,e,\beta}}{\partial a} = \frac{(\partial Z)_{c,e,\beta}}{\partial a} - \frac{(\partial \ln Z)_{c,e,\beta}}{\partial a} + \frac{\dfrac{\partial(a.\ln(V - k_0\beta)/\ln(V+e))_{c,e,\beta}}{RT(k_0\beta + e)}}{\partial a} \quad (4.105)$$

We have

$$\frac{(\partial Z)_{c,e,\beta}}{\partial a} = \frac{-V}{RT(V+e)(V-k_0\beta)} \quad (4.106)$$

$$\frac{(\partial \ln Z)_{c,e,\beta}}{\partial a} = \frac{(\partial \ln P)_{c,e,\beta}}{\partial a} = \frac{1}{P}\frac{(\partial P)_{c,e,\beta}}{\partial a} = \frac{(-V)}{P[V(V+e)(V-k_0\beta)]} \quad (4.107)$$

$$\frac{\partial}{\partial a}\left[\frac{a}{RT(k_0\beta+e)} \cdot \ln\frac{V-k_0\beta}{(V+e)}\right]_{c,e,\beta} = \frac{\ln[(V-k_0\beta)/(V+e)]}{RT(k_0\beta+e)} \quad (4.108)$$

and

$$\frac{(\partial \ln \varnothing)_{c,e,\beta}}{\partial a} = \frac{-V}{RT(V+e)(V-k_0\beta)} + \frac{1}{P(V+e)(V-k_0\beta)}$$

$$+ \frac{\ln[(V-k_0\beta)/(V+e)]}{RT(k_0\beta+e)} \quad (4.109)$$

$$\frac{(\partial \ln \varnothing)_{a,\beta,c}}{\partial e} = \frac{(\partial z)_{a,\beta,c}}{\partial e} - \frac{(\partial \ln Z)_{a,\beta,c}}{\partial e}$$

$$+ \frac{\partial}{\partial e}\frac{a}{RT(k_0\beta+e)}\left[\ln[(V-k_0\beta)/(V+e)]\right]_{a,\beta,c}$$

$$+ \frac{\partial}{\partial e}\left[\frac{k_0\beta}{RT}\left[\frac{\ln(V - k_0\beta)}{(k_0\beta)^2 + (k_0\beta e)} + \frac{\ln(V+e)}{e^2 + k_0\beta e} - \frac{\ln V}{k_0\beta e}\right]_{a,\ \beta,c}\right] \quad (4.110)$$

$$\frac{(\partial Z)_{a,\ \beta,c}}{\partial e} = \frac{-aV}{RT\,(V - k_0\beta)}\left[\frac{-1}{(V+e)^2}\left[-\frac{k_0\beta c}{RT\,(V - k_0\beta)}\right]\frac{-1}{(V+e)^2}\right] \quad (4.111)$$

Then

$$\frac{(\partial Z)_{a,\ \beta,c}}{\partial e} = \frac{aV + k_0\beta c}{RT\,(V - k_0\beta)(V+e)^2} \quad (4.112)$$

and

$$\frac{(\partial \ln Z)_{a,\ \beta,c}}{\partial e} = \frac{(\partial \ln P)_{a,\ \beta,c}}{\partial e} = \frac{1}{P} \cdot \frac{(\partial P)_{a,\ \beta,c}}{\partial e} \quad (4.113)$$

$$= \frac{1}{P}\left(-(aV + k_0\beta c)/(V.(V - k_0\beta))\right)\left(\frac{-1}{(V+e)^2}\right)$$

$$= \frac{1}{P}\left((aV + k_0\beta c)/(V.(V - k_0\beta).(V+e)^2)\right) \quad (4.114)$$

find value of

$$\frac{\partial}{\partial e}\left[\frac{a}{RT(k_0\beta+e)}\ln((V - k_0\beta)/(V+e))\right]_{a,\ \beta,c}$$

$$= \frac{a}{RT(k_0\beta+e)}\left[\frac{(k_0\beta - V).(V+e)}{(V - k_0\beta)(V+e)^2}\right] + \frac{\ln(V - k_0\beta)}{(V+e)} \cdot \frac{-aRT}{R^2T^2(k_0\beta+e)^2}$$

$$= \frac{a}{RT(k_0\beta+e)}\left[\frac{(k_0\beta - V)}{(V - k_0\beta)(V+e)} - \frac{\ln((V - k_0\beta)/(V+e))}{(k_0\beta+e)}\right] \qquad (4.115)$$

$$\frac{\partial}{\partial e}\left[\frac{k_0\beta c}{RT}\left[\frac{\ln(V - k_0\beta)}{(k_0\beta)^2 + (k_0\beta e)} + \frac{\ln(V+e)}{e^2 + k_0\beta e} - \frac{\ln V}{k_0\beta e}\right]\right]_{a,\ \beta,c}$$

$$= \frac{k_0\beta c}{RT}\left[\left[\frac{-\ k_0\beta}{((k_0\beta)^2 + (k_0\beta e))^2}\ln(V - k_0\beta)\right] + \right.$$

$$\left.\left[\frac{1}{(V+e)(e^2 + k_0\beta e)} - \frac{(2e + k_0\beta)\ln(V+e)}{(e^2 + k_0\beta e)^2}\right] + \frac{\ln V}{k_0\beta e^2}\right] \qquad (4.116)$$

find

$$\frac{(\partial \ln \varnothing)_{a,\ \beta,c}}{\partial e} = \frac{aV + k_0\beta c}{RT(V - k_0\beta)(V+e)^2} - \frac{1}{P}\left[\frac{(aV + k_0\beta c)}{V(V - k_0\beta)(V+e)^2}\right]$$

$$+ \frac{a}{RT(k_0\beta+e)}\left[\frac{(k_0\beta - V)}{(V - k_0\beta)(V+e)} - \frac{\ln((V - k_0\beta)/(V+e))}{(k_0\beta+e)}\right]$$

$$+ \frac{k_0\beta c}{RT}\left[\frac{-k_0\beta\ \ln(V - k_0\beta)}{((k_0\beta)^2 + (k_0\beta e))^2} + \frac{1}{(V+e)(e^2 + k_0\beta e)} - \frac{(2e + k_0\beta)\ln(V+e)}{(e^2 + k_0\beta e)^2} + \frac{\ln V}{k_0\beta e^2}\right] \qquad (4.117)$$

Begin with

$$\beta = y_i\beta_i + y_j\beta_j \tag{4.118}$$

$$= \frac{n_i}{n_i+n_j}\cdot\beta_i + \frac{n_j}{n_i+n_j}\cdot\beta_j$$

$(y_i = n_i/n,\ y_j = n_j/n,\ n = n_i+n_j)$

$$\frac{(\partial\beta)n_j}{\partial n_i} = \left[\frac{(n_i+n_j)-n_i}{(n_i+n_j)^2}\right]\beta_i + \left[\frac{n_j}{(n_i+n_j)^2}\right]\beta_j \tag{4.119}$$

$$= \frac{(\beta_i - \beta_j)\cdot n_j}{(n_i+n_j)^2}$$

$$\frac{(\partial\beta)n_j}{\partial n_i} = \frac{(\beta_i - \beta_j)\cdot y_i}{n} \tag{4.120}$$

for $e = y_i e_i + y_j e_j$ (4.121)

$$\frac{(\partial e)n_j}{\partial n_i} = \frac{(e_i - e_j)\cdot y_i}{n} \tag{4.122}$$

and $c = y_i^2 c_i + 2 y_i y_j c_i^{0.5} c_j^{0.5} + y_j^2 c_j$ (4.123)

$$\frac{(\partial c)n_j}{\partial n_i} = \frac{2y_i c_i (\partial y_i)n_j}{\partial n_i} + 2c_i^{0.5}c_j^{0.5} y_i \frac{(\partial y_i)n_j}{\partial n_i} \tag{4.124}$$

$$+ y_i \frac{(\partial y_i)n_j}{\partial n_i} + 2 y_i c_j \frac{(\partial y_j)n_j}{\partial n_i}$$

so $$\frac{(\partial c)n_j}{\partial n_i} = \frac{2 c_i y_i y_j + 2c_i^{0.5}c_j^{0.5}(y_j^2 - y_i y_j) - 2c_j y_j^2}{N} \tag{4.125}$$

next

$$a = y_i^2 c_i + 2 y_i y_j a_i^{0.5} a_j^{0.5} + y_j^2 a_j \quad (4.126)$$

$$\frac{(\partial a)_{n_j}}{\partial n_i} = \frac{2 a_i y_i y_j + 2 a_i^{0.5} a_j^{0.5} (y_i^2 - y_i y_j) - 2 a_j y_j^2}{N} \quad (4.127)$$

We have

$$\ln \varnothing_i = \ln \varnothing + \frac{n\ (\partial \ln \varnothing)_{nj,T,P}}{\partial n_i} \quad (4.128)$$

$$= \ln \varnothing + \frac{(\partial \ln \varnothing)_{a,e,c}}{\partial \beta} \cdot \frac{n\ (\partial \beta)_{nj}}{\partial n_i}$$

$$+ \frac{(\partial \ln \varnothing)_{a,e,\beta}}{\partial c} \cdot \frac{n\ (\partial c)_{nj}}{\partial n_i}$$

$$+ \frac{(\partial \ln \varnothing)_{a,\beta,c}}{\partial a} \cdot \frac{n\ (\partial a)_{nj}}{\partial n_i}$$

$$+ \frac{(\partial \ln \varnothing)_{a,\beta,c}}{\partial e} \cdot \frac{n\ (\partial e)_{nj}}{\partial n_i}$$

by

$$\ln \varnothing = Z - 1 - \ln Z + \frac{\ln V + \beta k_1}{(V - k_0 \beta)} + \frac{a}{RT(e + k_0 \beta)} \cdot \frac{\ln (V - k_0 \beta)}{(V + e)}$$

$$+\frac{k_0\beta c}{RT}\left[\frac{\ln(V-k_0\beta)}{(k_0\beta)^2+(k_0\beta e)}+\frac{\ln(V+e)}{(e^2+k_0\beta e)}-\frac{\ln V}{k_0\beta c}\right] \tag{4.129}$$

$$\frac{(\partial\ln\varnothing)_{a,e,c}}{\partial\beta}=\frac{V}{(V-k_0\beta)}\left[\frac{k_0+k_1}{(V-k_0\beta)}+\frac{2k_0k_1\beta}{(V-k_0\beta)^2}\right]$$

$$-\frac{V}{(V-k_0\beta)RT}\left[\frac{k_0c}{V(V+e)}+\frac{ak_0}{(V+e)(V-k_0\beta)}+\frac{k_0^2\beta c}{V(V+e(V-k_0\beta))}\right]$$

$$-\frac{1}{P}\left[\frac{RT(k_0+k_1)}{(V-k_0\beta)^2}+\frac{2k_0k_1\beta RT}{(V-k_0\beta)^3}-\frac{k_0c}{V(V+e)(V-k_0\beta)}-\frac{k_0(aV+k_0\beta c)}{V(V+e)(V-k_0\beta)}\right]$$

$$+\frac{(k_0+k_1)}{(V-k_0\beta)}+\frac{\beta k_0k_1}{(V-k_0\beta)^2}-\frac{ak_0}{RT(e+k_0\beta)}\frac{1}{(V-k_0\beta)}+\left[\frac{\ln((V-k_0\beta)/(V+e))}{(e+k_0\beta)}\right]$$

$$+\frac{k_0c}{RT}\left[\frac{\ln(V-k_0\beta)}{(k_0\beta)^2+(k_0\beta e)}+\frac{\ln(V+e)}{(e^2+k_0\beta e)}-\frac{\ln V}{k_0\beta e}\right]$$

$$+\frac{k_0^2\beta ce}{RT}\left[\frac{\ln V}{(k_0\beta e)^2}-\frac{1}{(V-k_0\beta)((k_0\beta)^2+(k_0\beta e))}-\frac{\ln(V+e)}{(e^2+k_0\beta e)^2}\right]$$

$$-\frac{k_0 \beta c}{RT} \cdot \frac{(\ln(V - k_0 \beta)).(2k_0^2 \beta + k_0 e)^2}{((k_0 \beta)^2 + (k_0 \beta e))^2} \qquad (4.130)$$

$$\frac{n(\partial\beta)_{nj}}{\partial n_i} = (\beta_i - \beta_j)\, y_j \qquad (4.131)$$

$$\left(\frac{\partial \ln \phi}{\partial c}\right)_{a,\beta,c} = \frac{(k_0\beta)}{(V - k_0\beta)(V+e)} \cdot \left[\frac{1}{PV} - \frac{1}{RT}\right] + \frac{k_0\beta}{RT}\left[\frac{\ln(V - k_0\beta)}{(k_0\beta)^2 + (k_0\beta e)} + \frac{\ln(V+e)}{(e^2 + k_0\beta e)} - \frac{\ln V}{k_0\beta e}\right] \qquad (4.132)$$

$$n\frac{\partial c}{\partial n_j} = 2\, c_i\, y_i\, y_j + 2\, c_i\, c_j\, (y_j^2 - y_i\, y_j) - 2c_i\, y_j^2 \qquad (4.133)$$

$$\left(\frac{\partial \ln \phi}{\partial a}\right)_{e,\beta,c} = \frac{-V}{RT(V+e)(V - k_0\beta)} + \frac{1}{P(V+e)(V - k_0\beta)} + \ln\left[\frac{(V - k_0\beta)}{(V+e)}\right] \cdot \frac{1}{RT(k_0\beta + e)} \qquad (4.134)$$

$$n\frac{\partial a}{\partial n_j} = 2\, a_i\, y_i\, y_j + 2\, a_i\, a_j\, (y_j^2 - y_i\, y_j) - 2a_i\, y_j^2 \qquad (4.135)$$

$$\left(\frac{\partial \ln \phi}{\partial e}\right)_{a,\beta,c} = \frac{aV + \beta k_0 c}{RT(V+e)^2 (V - k_0\beta)} - \frac{1}{P}\left[\frac{aV + \beta k_0 c}{V(V+e)^2 (V - k_0\beta)}\right] + \frac{a}{RT(k_0\beta + e)}$$
$$\left[\frac{(k_0\beta - V)}{(V+e)(V - k_0\beta)} - \ln\left[\frac{(V - k_0\beta)}{(V+e)}\right] \cdot \left[\frac{1}{(k_0\beta + e)}\right]\right] + \frac{\beta k_0 c}{RT}$$
$$\left[\frac{-k_0\beta \ln(V - k_0\beta)}{(k_0\beta)^2 + (k_0\beta e)} + \frac{1}{(V+e)(e^2 + k_0\beta e)} - \frac{(2e + \beta k_0 c)\ln(V+e)}{(e^2 + k_0\beta e)^2} + (\ln V)/(k_0\beta e)^2\right] \qquad (4.136)$$

$$\frac{n(\partial e)}{\partial n_j} = (e_i - e_j)\, y_j \quad (4.137)$$

4.5.3 $\frac{\partial \hat{\phi}^L_i}{\partial P}$ and $\frac{\partial \hat{\phi}^V_i}{\partial P}$

$$\frac{\partial(\hat{\phi}^v 1)}{\partial P} = \frac{\partial(\hat{\phi}^v 1)}{\partial V^v} \cdot \frac{\partial V^v}{\partial P} \quad (4.138)$$

$$\frac{\partial(\hat{\phi}^l 1)}{\partial P} = \frac{\partial(\hat{\phi}^l 1)}{\partial V^l} \cdot \frac{\partial V^l}{\partial P} \quad (4.139)$$

$$\hat{\phi}^l 1 = \exp\left[\left(\ln\phi^l 1 + n\frac{\partial(\ln\phi^l 1)}{\partial n_i}\right) n_j\right] \quad (4.140)$$

$$\frac{\partial(\hat{\phi}^l 1)}{\partial V^l} = \exp\left[\left(\ln\phi^l 1 + n\frac{\partial(\ln\phi^l 1)}{\partial n_i}\right) n_j\right] \cdot \frac{\partial\left(\ln\phi^l 1 + n\partial(\ln\phi^l 1)\right) n_j}{\partial V^l} \quad (4.141)$$

$$\frac{\partial\left(\ln\phi^l 1 + n\partial(\ln\phi 1)\right) n_j}{\partial V^l} = \frac{\partial \ln\phi^l 1}{\partial V^l} + \frac{\partial\left(n\,\partial(\ln\phi 1)/\partial n_i)n_j\right)}{\partial V^l} \quad (4.142)$$

$$\frac{\ln\phi^l 1}{\partial V^l} = \frac{\partial(Z^L)}{\partial V^l} + \frac{\partial \ln Z}{\partial V^l} + \frac{\partial \ln(V/(V-k_0\beta))}{\partial V^l} + \frac{\partial(k_1\beta/(V-k_0\beta))}{\partial V^l} + \frac{\partial\left((a/(RT(k_0\beta+e)))\ln((V-k_0\beta)/(V+e))\right)}{\partial V^l} + \frac{\partial}{\partial V^l}\left[(k_0\beta c/T)\left[\frac{\ln(V-k_0\beta)}{(k_0\beta)^2+(k_0\beta e)} + \frac{\ln(V+e)}{(e^2+k_0\beta e)} - \frac{\ln V}{k_0\beta e}\right]\right] \quad (4.143)$$

$$\frac{\partial z'}{\partial v'} = -\frac{k_0\beta}{(V-k_0\beta)^2} + k_1\beta\left[\frac{1}{(V-k_0\beta)^2} - \frac{2V}{(V-k_0\beta)^2}\right] - \frac{a}{RT}\left[\frac{1}{(V+e)(V-k_0\beta)} - \frac{V(2V+e-k_0\beta)}{(V+e)^2(V-k_0\beta)^2}\right] - \frac{\beta k_0 c.}{RT}\left[\frac{-(2V+e-k_0\beta)}{(V+e)^2(V-k_0\beta)^2}\right] \quad (4.144)$$

$$\frac{\partial \ln Z}{\partial v'} = \frac{\partial \ln P}{\partial v'} + \frac{\partial \ln(V/RT)}{\partial v'} \quad (4.145)$$

$$= \frac{1}{P}\left[\frac{\partial \ln P}{\partial v'}\right] + \frac{1}{V} \quad (4.146)$$

$$\frac{\partial \ln Z}{\partial V^{L}} = \frac{1}{P}\left[\frac{-RT}{(V - k_0\beta)^2} - \frac{2\beta k_1 RT}{(V - k_0\beta)^3} + \frac{a(2V + e - k_0\beta)}{(V + e)^2 (V - k_0\beta)^2} + \frac{k_0\beta c(3V^2 + 2eV - 2k_0\beta V - k_0\beta e)}{V^2 (V + e)^2 (V - k_0\beta)^2}\right] + \frac{1}{V} \quad (4.147)$$

$$\frac{\partial \ln(V/(V - k_0\beta))}{\partial V^{L}} = \frac{-k_0\beta}{V(V - k_0\beta)} \quad (4.148)$$

$$\frac{\partial(\beta k_1/(V - k_0\beta))}{\partial V^{L}} = \frac{-\beta k_1}{(V - k_0\beta)^2} \quad (4.149)$$

$$\frac{\partial\ (a/(RT(k_0\beta + e).\ln(V - k_0\beta))}{\partial V^{L}\qquad (V + e)} = \frac{a}{RT(V - k_0\beta)(V + e)} \quad (4.150)$$

$$\frac{\partial}{\partial V^{L}}\left[\frac{k_0\beta c}{T}\left[\frac{\ln(V - k_0\beta)}{((k_0\beta)^2 + k_0\beta e)} + \frac{\ln(V + e)}{(e^2 + k_0\beta e)} - \frac{\ln V}{k_0\beta e}\right]\right]$$

$$= \frac{k_0\beta c}{RT}\left[\frac{1}{(V - k_0\beta)((k_0\beta)^2 + k_0\beta e)} + \frac{1}{(e^2 + k_0\beta e)(V + e)} - \frac{1}{V k_0\beta e}\right] \quad (4.151)$$

$$\frac{\partial \ln \varnothing^{L}}{\partial V^{L}} = \frac{-k_0\beta}{(V - k_0\beta)^2} + \beta k_1\left[\frac{1}{(V - k_0\beta)^2} - \frac{2V}{(V - k_0\beta)^3}\right]$$

$$- \frac{a}{RT}\left[\frac{1}{(V - k_0\beta)(V+e)} - \frac{V(2V + e - k_0\beta)}{(V - k_0\beta)^2(V+e)^2}\right]$$

$$- \frac{k_0\beta c}{RT} - \left[\frac{(2V + e - k_0\beta)}{(V - k_0\beta)^2(V+e)^2}\right]\left[- \frac{1}{V}\right.$$

$$\frac{-1}{P} - \left[\frac{RT}{(V - k_0\beta)^2} - \frac{2k_1\beta RT}{(V - k_0\beta)^3} + \frac{a(2V + e - k_0\beta)}{(V - k_0\beta)^2(V+e)^2}\right.$$

$$\left. + \frac{k_0\beta c(3V^2 + 2eV - 2k_0\beta V - k_0\beta e)}{V(V - k_0\beta)^2(V+e)^2}\right]$$

$$\frac{-k_0\beta}{V(V - k_0\beta)} - \frac{k_1\beta}{(V - k_0\beta)^2} + \frac{a}{RT(V - k_0\beta)(V+e)}$$

$$+ \frac{k_0\beta c}{RT}\left[\frac{1}{(V - k_0\beta)((k_0\beta)^2 + k_0\beta e)} + \frac{1}{(e^2 + k_0\beta e)(V+e)} - \frac{1}{V k_0\beta e}\right] \quad (4.152)$$

Let $[FBLV_1] = \dfrac{\partial(\ln \varnothing / \partial\beta)}{\partial\beta}$ (4.153)

$[FCLV_1] = \dfrac{\partial(\ln \varnothing / \partial c)}{\partial\beta}$ (4.154)

$[FALV_1] = \dfrac{\partial(\ln \varnothing / \partial a)}{\partial\beta}$ (4.155)

$[FELV_1] = \dfrac{\partial(\ln \varnothing / \partial e)}{\partial\beta}$ (4.156)

$$\frac{\partial}{\partial V^L}\left[\frac{n\,(\partial \ln \varnothing^L)}{\partial n_i}\right]_{nj} = (\beta_i - \beta_j)\, y_i\,[\,FBLV_1\,]$$

$$+ [\,2\,c_i\; y_i\, y_j\; + 2\,c_i^{0.5}\, c_j^{0.5}\,(\,y_j^2\; - y_i\, y_j\,) - 2\,c_j\, y_j\,][FCLV_1]$$

$$+ [\,2\,a_i\; y_i\, y_j\; + 2\,a_i^{0.5}\, a_j^{0.5}\,(\,y_j^2\; - y_i\, y_j\,) - 2\,a_j\, y_j\,][FALV_1]$$

$$+ (\;e_i\; - \;e_j\,)[FELV_1] \qquad (4.157)$$

$$FBLV_1 = \frac{V}{(V - k_0\beta)^3} \cdot \quad [\,-(\,k_0 \;+\; k_1\,) \;-\; \frac{4k_0\, k_1\beta]}{(V - k_0\,\beta)} \;-\; \frac{k_0\beta}{(V - k_0\,\beta)^3}\;[\,(\,k_0 \;+\; k_1\,) \;+\; \frac{2k_0k_1\beta]}{(V - k_0\,\beta)}$$

$$- \quad \frac{V}{RT(V - k_0\,\beta)} \quad - \left[\frac{k_0\beta c(2V+e)}{V^2\,(V+e)^2} \;-\; \frac{ak_0\,(\,2V \;+\; e - k_0\beta\,)}{(V - k_0\,\beta)^2(V+e)^2}\right.$$

$$\left. - \quad \frac{k_0^2\beta c\,(3V^2+2eV - 2k_0\beta V - k_0\beta e)}{V^2\,(V - k_0\,\beta)^2(V+e)^2}\right] + \left[\frac{k_0\, c}{V(V+e)} \quad + \quad \frac{ak_0}{(V - k_0\,\beta)(V+e)}\right.$$

$$\left. + \quad \frac{k_0^2\beta c}{V(V - k_0\,\beta)(V+e)}\right] \cdot \left[\frac{k_0\beta}{(V - k_0\,\beta)^2\; RT}\right]$$

$$- \frac{1}{p}\left[\frac{-2RT(k_0 + k_1)}{(V - k_0\,\beta)^3} \;-\; \frac{6\,k_0k_1\beta RT}{(V - k_0\,\beta)^4} \;+\; \frac{k_0c(3V^2+2eV - 2k_0\beta V - k_0\beta e)}{V^2(V - k_0\,\beta)^2(V+e)^2}\right.$$

$$- k_0 \left[\frac{V(V - k_0 \beta)^2 (V + e) a \quad - \quad [aV + k_0 \beta e]}{V^2 (V - k_0 \beta)^2 (V + e)^4} \right] \Bigg]$$

$$- \left[\frac{RT(k_0 + k_1)}{(V - k_0 \beta)^3} + \frac{2k_0 k_1 \beta RT}{(V - k_0 \beta)^4} - \frac{k_0 c \,(V - k_0 \beta)}{V(V - k_0 \beta)^2 (V + e)} - \frac{k_0 (aV + k_0 \beta c)}{V(V - k_0 \beta)^2 (V + e)} \right] \frac{\partial (1/P)}{\partial V^L}$$

$$+ \left[\frac{- k_0}{(V - k_0 \beta)^2} \; \frac{-k_1}{(V - k_0 \beta)^2} - \frac{2k_0 k_1 \beta}{(V - k_0 \beta)^3} \; \frac{-ak_0}{RT \;\; (k_0 \beta + e)} \right] \left[\frac{-1}{(V - k_0 \beta)^2} + \frac{1}{(V - k_0 \beta)(V + e)} \right]$$

$$+ \frac{k_0 c}{RT} \left[\frac{1}{(V - k_0 \beta)((k_0 \beta)^2 + k_0 \beta e))} + \frac{1}{(V + e) \;\; (e^2 + k_0 \beta e)} - \frac{1}{V k_0 \beta e} \right]$$

$$+ \frac{k_0^{\,2} c \beta e}{RT} \left[\frac{1}{V(k_0 e \beta)^2} + \frac{1}{((k_0 \beta)^2 + k_0 \beta e))(V - k_0 \beta)^2} - \frac{1}{(V + e) \;\; (e^2 + k_0 \beta e)^2} \right]$$

$$- \; k_0 c \beta \left[\frac{2 \;\; \beta k_0^2 + k_0 e}{((k_0 \beta)^2 + k_0 \beta e))^2 (V - k_0 \beta)} \right] \qquad (4.158)$$

$$\frac{\partial (1/P)}{\partial V^L} = \frac{-1}{P} \frac{\partial P}{\partial V^L} \qquad (4.159)$$

$$\frac{\partial P}{\partial V^L} = - \frac{RT}{(V - k_0 \beta)^2} - \frac{2k_1 \beta RT}{(V - k_0 \beta)^3} + \frac{a(2V + e - k_0 \beta)}{(V - k_0 \beta)^2 (V + e)^2}$$

$$+ \frac{k_0 c(3V^2 + 2eV - 2k_0 \beta V - k_0 \beta e)}{V^3 (V - k_0 \beta)^2 (V + e)^2} \qquad (4.160)$$

$$FCLV_1 = \frac{k_0 \beta}{(V - k_0 \beta)(V + e)} \left[\frac{-1}{PV} - \frac{1}{VP^2} \frac{\partial P}{\partial V^L} \right] \left[- \frac{k_0 \beta (2V + e - k_0 \beta).}{(V - k_0 \beta)^2 (V + e)^2} \right.$$

$$\left[\frac{1}{PV} - \frac{1}{RT}\right] + \frac{k_0\beta c}{RT}\left[\frac{1}{(V - k_0\beta)((k_0\beta)^2 + k_0\beta e))} + \frac{1}{(e^2 + k_0\beta e)(V + e)} - \frac{1}{V k_0\beta e}\right] \quad (4.161)$$

$$FALV_1 = \frac{1}{RT}\left[\frac{V(2V+e- k_0\beta) - (V - k_0\beta)(V + e)}{(V - k_0\beta)^2(V + e)^2}\right]\left[+\frac{1}{RT (V - k_0\beta)(V + e)}\right.$$

$$- \frac{(2V+e- k_0\beta)P + (V - k_0\beta)(V + e)\frac{\partial P}{\partial V^L}}{P^2 (V - k_0\beta)^2(V + e)^2} \quad (4.162)$$

$$FELV_1 = \frac{a}{RT(V - k_0\beta)(V + e)} - \frac{(aV + k_0\beta c)(3V^2 + 2e + e^2 - 2 k_0\beta V)}{RT(V - k_0\beta)^2(V + e)^4}$$

$$- \frac{1}{P}\left[\frac{a}{V(V - k_0\beta)(V + e)^2}\right.$$

$$\left. - \frac{(aV + k_0\beta c)(4V^3 + 4eV + 2e^2V - 3k_0\beta V^2 - 2k_0\beta e - k_0\beta e^2)}{V^2(V - k_0\beta)^2(V + e)^4}\right]$$

$$+ \frac{1}{P^2}\left[\frac{(aV + k_0\beta c)}{V(V - k_0\beta)(V + e)^2}\right]\frac{\partial P}{\partial V^L} + a\left[\frac{-1}{(V - k_0\beta)(V + e)} + \frac{(2V- k_0\beta+e)}{(V - k_0\beta)(V + e)^2}\right.$$

$$\left.- \frac{(V - k_0)}{(V + e)^3}\right] + \frac{k_0\beta c}{RT}\left[\frac{- k_0\beta}{((k_0\beta)^2+k_0\beta e))^2(V - k_0\beta)} - \frac{1}{(e^2 + k_0\beta e)(V + e)^2}\right.$$

$$
- \frac{(V - k_0)}{(V + e)^3} + \Bigg] \frac{k_0 \beta c}{RT} \Bigg[\frac{- k_0 \beta}{((k_0 \beta)^2 + k_0 \beta e))^2 (V - k_0 \beta)} - \frac{1}{(e^2 + k_0 \beta e)(V + e)^2}
$$

$$
- \frac{(2e + k_0 \beta)}{(e^2 + k_0 \beta e)^2 (V + e)} + \frac{1}{k_0 \beta e^2 V} \Bigg] \qquad (4.163)
$$