9.5 Assuming that two pure fluids and their mixture can be described by the van der Waals equation of state,

$$P = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}^2}$$

and that for the mixture the van der Waals one-fluid mixing rules apply

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad \text{and} \quad b = \sum_i x_i b_i$$

a. Show that the fugacity coefficient for species i in the mixture is

$$Z = \frac{P\underline{V}}{RT}$$

$$\ln \phi_i = \ln \frac{\bar{f}_i}{x_i P} = \frac{B_i}{Z - B} - \ln(Z - B) - \frac{2\sum_j x_j a_{ij}}{RT\underline{V}}$$

where $B = Pb/RT$.

b. Derive an expression for the activity coefficient of each species.

lets Start with definition of fugacity Coeff,

$$\boxed{\ln \bar{\phi}_i = \ln \frac{\bar{f}_i(T, P, \underline{x})}{x_i P} = \frac{1}{RT} \int_{\underline{V}=\infty}^{\underline{V}=ZRT/P} \left[\frac{RT}{\underline{V}} - N \left(\frac{\partial P}{\partial N_i} \right)_{T,V,N_{j \neq i}} \right] d\underline{V} - \ln Z}$$

now going to our Eos

$$P = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}_2}$$

and "converting" molar volume to extensive volume

$$P = \frac{NRT}{V - Nb} - \frac{N^2 a}{V}$$

now we can Slap in the mixing rules version of a and b

$$P = \frac{NRT}{V - N\sum_i x_i b} - \frac{N^2 \sum\sum x_i x_j a_{ij}}{V^2}$$

now the $N x_i$ terms may become N_i by the def of x_i

$$P = \frac{NRT}{V - \sum N_i b_i} - \frac{\sum\sum N_i N_j a_{ij}}{V^2}$$

taking the partial wrt N_i @ const T, V

$$\left(\frac{\partial P}{\partial N_i}\right)_{V,T} = \frac{RT}{V - \sum N_i b_i} - \frac{NRT}{(V - \underbrace{\sum N_i b_i}_{b})^2}(-b_i) - \frac{2\sum N_j a_{ij}}{V^2}$$

$$= \frac{RT}{V - \sum N_i b_i} + \frac{NRT b_i}{(V - b)^2} - \frac{2\sum N_j a_{ij}}{V^2}$$

now go back to molar volume and b

$$\left(\frac{\partial P}{\partial N_i}\right)_{T,\underline{V}} = \frac{RT}{N(\underline{V} - b)} + \frac{NRT b_i}{N^2(\underline{V} - b)^2} - \frac{2N\sum x_j a_{ij}}{N^2 \underline{V}^2}$$

multiply by N

$$N\left(\frac{\partial P}{\partial N_i}\right)_{T,V} = \frac{RT}{\underline{V} - b} + \frac{RT b_i}{(\underline{V} - b)^2} - \frac{2\sum x_j a_{ij}}{\underline{V}^2}$$

so

$$\ln(\phi) = \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}=zRT/P}\left[\frac{RT}{\underline{V}} - N\left(\frac{\partial P}{\partial N_i}\right)_{T,V}\right] d\underline{V} - \ln(z)$$

$$= \frac{1}{RT} \int_{\underline{V}=\infty}^{\underline{V}=ZRT/P} \left[\frac{RT}{\underline{V}} - \frac{RT}{\underline{V}-b} - \frac{RT\, b_i}{(\underline{V}-b)^2} + \frac{2 \sum x_j a_{ij}}{\underline{V}^2} \right] d\underline{V} - \ln(Z)$$

$$= \frac{1}{RT} \left[RT \ln(\underline{V}) - RT \ln(\underline{V}-b) + \frac{RT\, b_i}{\underline{V}-b} - \frac{2 \sum x_j a_{ij}}{\underline{V}} \right]_{\underline{V}=\infty}^{\underline{V}=ZRT/P} - \ln(Z)$$

$$= \left[\ln\left(\frac{\underline{V}}{\underline{V}-b}\right) + \frac{b_i}{\underline{V}-b} - \frac{2 \sum x_j a_{ij}}{RT\, \underline{V}} \right]_{\underline{V}=\infty}^{\underline{V}=ZRT/P} - \ln(Z)$$

$$= \left[\ln\left(\frac{\frac{ZRT}{P}}{\frac{ZRT}{P} - b}\right) - 0 + \frac{b_i}{\frac{ZRT}{P} - b} - 0 - \frac{2 \sum x_j a_{ij}}{RT \frac{ZRT}{P}} + 0 \right] - \ln(Z)$$

$$= \ln(Z) - \ln\left(Z - \frac{Pb}{RT}\right) + \frac{\frac{Pb_i}{RT}}{Z - \frac{Pb}{RT}} - \frac{2 \sum x_j a_{ij}}{RT \frac{ZRT}{P}} - \ln(Z)$$

$\underline{V}$ from lim of integration

now remembering $B = \frac{Pb}{RT}$

$$\ln(\phi_i) = -\ln(Z - B) + \frac{B}{Z - B} - \frac{2 \sum x_i a_{ij}}{RT\, \underline{V}}$$

$$\frac{P\underline{V}}{RT} = Z$$

(B)

(B) we know the activity coefficient is

$$\gamma = \frac{\bar{f}_i^L}{x_i f_i^L}$$

and $\bar{f}_i^L = x_i P \exp\left[\text{answer to last question}\right]$

anddd $f_i^L = P \exp\left[(Z-1) - \ln(Z-B_i) - \frac{a_{ii}}{Z}\right]$

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$$\gamma = \frac{x_i P \exp\left[\frac{B}{Z-B} - \ln(Z-B) - \frac{2\sum x_i a_{ij}}{RT\,\underline{V}}\right]}{x_i P \exp\left[(Z-1) - \ln(Z-B_i) - \frac{a_{ii}}{Z}\right]}$$

$$\gamma = \frac{\exp\left[\frac{B}{Z-B} - \ln(Z-B) - \frac{2\sum x_i a_{ij}}{RT\,\underline{V}}\right]}{\exp\left[(Z-1) - \ln(Z-B_i) - \frac{a_{ii}}{Z}\right]}$$