VLE from an Equation of State

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FUGACITY IN A MIXTURE BY AN EQUATION OF STATE

$$d\underline{G} = \underline{V}dP - \underline{S}dT + \sum_i \left(\partial \underline{G} / \partial n_i \right)_{T,P,n_{j\neq i}} dn_i$$

and noting,

$$d\underline{A} = -Pd\underline{V} - \underline{S}dT + \sum_i \left(\partial \underline{A} / \partial n_i \right)_{T,\underline{V},n_{j\neq i}} dn_i$$

we may substitute

$$d\underline{A} = d\underline{G} - Pd\underline{V} - \underline{V}dP = \underline{V}dP - \underline{S}dT + \sum_i \left(\partial \underline{G} / \partial n_i \right)_{T,P,n_{j\neq i}} dn_i - Pd\underline{V} - \underline{V}dP$$

$$\Rightarrow -Pd\underline{V} - \underline{S}dT + \sum_i \left(\partial \underline{A} / \partial n_i \right)_{T,\underline{V},n_{j\neq i}} dn_i = -Pd\underline{V} - \underline{S}dT + \sum_i \left(\partial \underline{G} / \partial n_i \right)_{T,P,n_{j\neq i}} dn_i$$

Equating coefficients of dn_i

$$\left(\partial \underline{A} / \partial n_i \right)_{T,\underline{V},n_{j\neq i}} = \left(\partial \underline{G} / \partial n_i \right)_{T,P,n_{j\neq i}} = \mu_i(T,P,\underline{V})$$

Referencing to the ideal gas state:

$$\ln(\hat{f}_i / y_i P) = (\mu_i(T,P) - \mu_i^{ig}(T,P))/RT = \left(\frac{\partial(\underline{A} - \underline{A}^{ig})/RT}{\partial n_i} \right)_{T,\underline{V},n_{j\neq i}} - \ln Z$$

K-Values from an Equation of State

To apply this, consider the PR EOS as an example.

$$\frac{\underline{A}-\underline{A}^{ig}}{nRT} = -ln(1-B/Z) - \frac{A}{B\sqrt{8}} ln\left(\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B}\right) = -ln(1-b\rho) - \frac{a}{bRT\sqrt{8}} ln\left(\frac{1+(1+\sqrt{2})b\rho}{1+(1-\sqrt{2})b\rho}\right)$$

For "random mixing", the probability of any "*i-j* interaction" is the same and goes as the product of the "i-j concentrations". This suggests that we could define $A^v = \Sigma\Sigma y_i y_j A_{ij}$ and $B^v = \Sigma y_i B_i$ letting $A_{ij}=\sqrt{A_{ii}A_{jj}}$ by comparison to the form of the energy equation for mixtures (discussed below). Then differentiation (as detailed below) yields

$$ln\left(\frac{\hat{f}_i^v}{y_i P}\right) = \frac{B_i^v}{B^v}(Z^v - 1) - ln(Z^v - B^v) - \frac{A^v}{B^v\sqrt{8}} ln\left(\frac{Z^v+(1+\sqrt{2})B^v}{Z^v+(1-\sqrt{2})B^v}\right)\left(\frac{2\Sigma y_j A_{ij}}{A^v} - \frac{B_i^v}{B^v}\right)$$

Note: $A^L = \Sigma\Sigma x_i x_j A_{ij}$ and $B^L = \Sigma x_i B_i$ but the derivation of the fugacity coefficient would be the same and:

$$ln\left(\frac{\hat{f}_i^L}{x_i P}\right) = \frac{B_i^L}{B^L}(Z^L - 1) - ln(Z^L - B^L) - \frac{A^L}{B^L\sqrt{8}} ln\left(\frac{Z^L+(1+\sqrt{2})B^L}{Z^L+(1-\sqrt{2})B^L}\right)\left(\frac{2\Sigma x_j A_{ij}}{A^L} - \frac{B_i^L}{B^L}\right)$$

As we saw in the case of pure fluids, there is no fundamental reason to distinguish between the vapor and liquid phases except by the initial guess for *Z*. The equation of state approach encompasses this lack of distinction in a very direct way. To obtain an expression for K_i, it is convenient to define the fugacity coefficients of a mixture as

$$\frac{\hat{f}_i^v}{y_i P} \equiv \hat{\varphi}_i^v \quad and \quad \frac{\hat{f}_i^L}{x_i P} \equiv \hat{\varphi}_i^L$$ ⇒ Recalling that $\hat{f}_i^v = \hat{f}_i^L$ at equilibrium, we find that $K_i = \hat{\varphi}_i^L / \hat{\varphi}_i^v$

FUGACITY IN A MIXTURE BY AN EQUATION OF STATE: Density Dependent Formulas

Example. Fugacity coefficient for the virial equation

For pressures to 10 bars, a common method is to use the virial equation given by: $Z = 1 + B\rho$; where $B = \Sigma\Sigma y_i y_j B_{ij}$ and $B_{ij} = \sqrt{B_{ii} B_{jj}}$. Develop an expression for the fugacity coefficient.

$$ln(\varphi_k) = \left(\frac{\partial(\underline{A} - \underline{A}^{ig})/RT}{\partial n_k}\right)_{T,\underline{V},n_{k\neq i}} - ln Z; \quad \frac{\underline{A} - \underline{A}^{ig}}{nRT} = \int_0^{B\rho} B\rho \frac{dB\rho}{B\rho} = B\rho \Rightarrow \frac{\underline{A} - \underline{A}^{ig}}{RT} = \frac{Bn^2}{V} = \frac{1}{V}\sum\sum n_i n_j B_{ij}$$

Note: For $B_{ij} = \sqrt{B_{ii} B_{jj}}$, $\sum\sum n_i n_j B_{ij} = \left(\sum n_i \sqrt{B_{ii}}\right)\left(\sum n_j \sqrt{B_{jj}}\right) = \left(\sum n_j \sqrt{B_{jj}}\right)^2$

$$\left(\frac{\partial(\underline{A} - \underline{A}^{ig})/RT}{\partial n_k}\right)_{T,\underline{V},n_{k\neq i}} = \frac{1}{V}\frac{\partial\left(\sum n_j \sqrt{B_{jj}}\right)^2}{\partial n_k} = \frac{2\left(\sum n_j \sqrt{B_{jj}}\right)}{V}\frac{\partial\left(\sum n_j \sqrt{B_{jj}}\right)}{\partial n_k}$$

$$\frac{\partial\left(\sum n_j \sqrt{B_{jj}}\right)}{\partial n_k} = \sqrt{B_{kk}} \Rightarrow \ln(\varphi_k) = \frac{2}{V}\sqrt{B_{kk}}\left(\sum n_j \sqrt{B_{jj}}\right) - \ln Z = 2\rho\left(\sum y_j B_{jk}\right) - \ln Z$$

Example. Fugacity coefficient for the van der Waals EOS

The VdW EOS provides a simple but fairly accurate representation of key EOS concepts for mixtures. The main tricks developed for this EOS are the same for other EOS's but the algebra is a little simpler.

$$Z = \frac{1}{1-b\rho} - \frac{a\rho}{RT}$$

where $a = \Sigma\Sigma y_i y_j a_{ij}$; $a_{ij} = \sqrt{a_{ii} a_{jj}}$

$b = \Sigma y_i b_i$

Develop an expression for the fugacity coefficient.

Solution

$$ln(\varphi_k) = \left(\frac{\partial(\underline{A} - \underline{A}^{ig})/RT}{\partial n_k}\right)_{T,\underline{V},n_{k\neq i}} - ln\,Z$$

$$\frac{\underline{A} - \underline{A}^{ig}}{nRT} = \int_0^{b\rho} (Z-1)\frac{d(b\rho)}{b\rho} = \int_0^{b\rho}\left(\frac{b\rho}{1-b\rho} - \frac{a}{bRT}b\rho\right)\frac{d(b\rho)}{b\rho} = -ln(1-b\rho) - \frac{a}{bRT}b\rho$$

$$\frac{\underline{A} - \underline{A}^{ig}}{RT} = -n\,ln(1-b\rho) - \frac{an^2}{\underline{V}RT} = -n\,ln(1-b\rho) - \frac{\sum\sum n_i n_j a_{ij}}{\underline{V}RT}$$

$$\left(\frac{\partial(\underline{A}-\underline{A}^{ig})/RT}{\partial n_k}\right)_{T,\underline{V},n_{k\neq i}} = -ln(1-b\rho)+\frac{n}{1-b\rho}\left(\frac{\partial b\rho}{\partial n_k}\right)-\frac{1}{\underline{V}RT}\frac{\partial(\Sigma\Sigma n_i n_j a_{ij})}{\partial n_k}$$

$$b\rho = \frac{n\left(\sum y_j\sqrt{b_j}\right)}{\underline{V}} = \frac{\left(\sum n_j\sqrt{b_j}\right)}{\underline{V}} \Rightarrow \frac{\partial b\rho}{\partial n_k} = \frac{b_k}{\underline{V}}$$

Note: For $a_{ij}=\sqrt{a_{ii}a_{jj}}$, $\sum\sum n_i n_j a_{ij} = \left(\sum n_i\sqrt{a_{ii}}\right)\left(\sum n_j\sqrt{a_{jj}}\right) = \left(\sum n_j\sqrt{a_{jj}}\right)^2$

$$\frac{\partial(\Sigma\Sigma n_i n_j a_{ij})}{\partial n_k} = \frac{\partial\left(\sum n_j\sqrt{a_{jj}}\right)^2}{\partial n_k} = 2\sqrt{a_{kk}}\left(\sum n_j\sqrt{a_{jj}}\right)$$

$$\ln(\varphi_k) = -\ln(1-b\rho)+\frac{n}{1-b\rho}\left(\frac{b_k}{V}\right)-\frac{2\Sigma n_j a_{kj}}{VRT}-\ln Z = -\ln(1-b\rho)+\frac{b_k\,\rho}{1-b\rho}-\frac{2\,\rho\Sigma x_j a_{kj}}{RT}-\ln Z$$

$$b\rho \equiv \frac{B}{Z}; \quad \frac{a}{bRT}\equiv\frac{A}{B}; \quad \frac{a_{jk}}{a}\equiv\frac{A_{jk}}{A}; \quad \frac{b_k}{b}\equiv\frac{B_k}{B}$$

$$\ln(\varphi_k) = -\ln(Z-B)+\frac{B_k}{Z-B}-\frac{2\Sigma x_j A_{kj}}{Z}$$

Example. Fugacity coefficient for the PREOS

$$Z = \frac{1}{1-b\rho} - \frac{a\rho}{RT}\frac{1}{\left(1+2b\rho - b^2\rho^2\right)}$$

where $a = \Sigma\Sigma y_i y_j a_{ij}$; $a_{ij} = \sqrt{a_{ii} a_{jj}}$

$b = \Sigma y_i b_i$

Develop an expression for the fugacity coefficient.

Solution

$$ln(\varphi_k) = \left(\frac{\partial(\underline{A} - \underline{A}^{ig})/RT}{\partial n_k}\right)_{T,\underline{V},n_{k\neq i}} - ln\,Z$$

From our integration for the pure fluid,

$$\left(\frac{\underline{A} - \underline{A}^{ig}}{nRT}\right) = -ln(1-b\rho) - \frac{a}{bRT\sqrt{8}}\,ln\left(\frac{1+(1+\sqrt{2})b\rho}{1+(1-\sqrt{2})b\rho}\right)$$

$$\left(\frac{\underline{A} - \underline{A}^{ig}}{RT}\right) = -n\,ln(1-b\rho) - \frac{an^2}{nbRT\sqrt{8}}\left\{ln\left[1+(1+\sqrt{2})b\rho\right] - ln\left[1+(1-\sqrt{2})b\rho\right]\right\}$$

$$\left(\frac{\partial(\underline{A}-\underline{A}^{ig})/RT}{\partial n_k}\right)_{T,V,n_{k\neq i}} = -ln(1-b\rho)+\frac{n}{1-b\rho}\left(\frac{\partial b\rho}{\partial n_k}\right)-\frac{an^2}{nbRT\sqrt{8}}\left\{\frac{(1+\sqrt{2})\left(\frac{\partial b\rho}{\partial n_k}\right)}{1+(1+\sqrt{2})b\rho}-\frac{(1-\sqrt{2})\left(\frac{\partial b\rho}{\partial n_k}\right)}{1+(1-\sqrt{2})b\rho}\right\}$$

$$-\ln\left[\frac{1+(1+\sqrt{2})b\rho}{1+(1-\sqrt{2})b\rho}\right]\left[\frac{\left(\frac{\partial an^2}{\partial n_k}\right)}{nbRT\sqrt{8}}-\frac{an^2}{RT\sqrt{8}}\frac{\left(\frac{\partial nb}{\partial n_k}\right)}{(nb)^2}\right]$$

$$b\rho = \frac{n\left(\sum x_j\sqrt{b_j}\right)}{\underline{V}} = \frac{\left(\sum n_j\sqrt{b_j}\right)}{\underline{V}} \Rightarrow \frac{\partial b\rho}{\partial n_k} = \frac{b_k}{\underline{V}}$$

Note: For $a_{ij}=\sqrt{a_{ii}a_{jj}}$, $\sum\sum n_i n_j a_{ij} = \left(\sum n_i\sqrt{a_{ii}}\right)\left(\sum n_j\sqrt{a_{jj}}\right) = \left(\sum n_j\sqrt{a_{jj}}\right)^2$

$$\frac{\partial(an^2)}{\partial n_k} = \frac{\partial(\Sigma\Sigma n_i n_j a_{ij})}{\partial n_k} = \frac{\partial\left(\sum n_j\sqrt{a_{jj}}\right)^2}{\partial n_k} = 2\sqrt{a_{kk}}\left(\sum n_j\sqrt{a_{jj}}\right)$$

$$\ln(\varphi_k) = -\ln(1-b\rho) - \ln Z + \frac{b_k\,\rho}{1-b\rho} - \frac{ab_k\,\rho}{bRT\sqrt{8}}\left\{\frac{(1+\sqrt{2})}{1+(1+\sqrt{2})b\rho} - \frac{(1-\sqrt{2})}{1+(1-\sqrt{2})b\rho}\right\}$$

$$-\frac{a}{bRT\sqrt{8}}\ln\left[\frac{1+(1+\sqrt{2})b\rho}{1+(1-\sqrt{2})b\rho}\right]\left[\frac{2\Sigma x_j a_{jk}}{a} - \frac{b_k}{b}\right]$$

Note:

$$\frac{b_k\,\rho}{1-b\rho} - \frac{ab_k\,\rho}{bRT\sqrt{8}}\left[\frac{(1+\sqrt{2})}{1+(1+\sqrt{2})b\rho} - \frac{(1-\sqrt{2})}{1+(1-\sqrt{2})b\rho}\right] = \frac{b_k}{b}\left\{\frac{b\rho}{1-b\rho} - \frac{ab\rho}{bRT\sqrt{8}}\left[\frac{1}{1+2b\rho-b^2\rho^2}\right]\right\} = \frac{b_k}{b}\{Z-1\}$$

$$\ln(\varphi_k) = -\ln(1-b\rho) - \ln Z + \frac{b_k}{b}\{Z-1\} - \frac{a}{bRT\sqrt{8}}\ln\left[\frac{1+(1+\sqrt{2})b\rho}{1+(1-\sqrt{2})b\rho}\right]\left[\frac{2\Sigma x_j a_{jk}}{a} - \frac{b_k}{b}\right]$$

$$b\rho \equiv \frac{B}{Z}; \quad \frac{a}{bRT} \equiv \frac{A}{B}; \quad \frac{a_{jk}}{a} \equiv \frac{A_{jk}}{A}; \quad \frac{b_k}{b} \equiv \frac{B_k}{B}$$

$$\ln(\varphi_k) = -\ln(Z-B) + \frac{B_k}{B}\{Z-1\} - \frac{A}{B\sqrt{8}}\ln\left[\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B}\right]\left[\frac{2\Sigma x_j A_{jk}}{A} - \frac{B_k}{B}\right]$$

Example 10.6. Bubble point pressure from PR EOS

Use the PREOS(k_{ij} = 0) to determine the bubble point pressure of equimolar solution of nitrogen+methane at 100K.

Solution:

Initial guess $P \approx \Sigma x_i P_i^{vap} \approx .5*7.851+.5*.340 = 4.1$ bars; $y_1^{is} = .5*7.851/4.1=.96$

						p=4.1,y1=.963		p=4.5,y1=.944		p=4.24,y1=.945	
Comp	Tc	Pc	ω	Tb	x	K	y	K	y	K	y
N2	126.2	33.94	.040	77	.5	1.95	.970	1.796	.898	1.893	.9467
CH4	190.2	46.00	.011	112	.5	.115	.057	.1046	.052	.1097	.0548
							1.027		0.950		1.0015

Note: y_1 for next guess is computed from estimate of y_1 of current guess. For example, 0.944=0.970/1.027, and 0.945=0.898/0.950. Note how quickly the estimate for y_1 converges to the final estimate of 0.945.

Example 10.7. Flash of PREOS solutions

A distillation is to produce overhead products having the following compositions:

	Propane	Isobutane	n-Butane
z_i	0.23	0.67	0.10

Suppose only a partial condensation at 320 K and 8 bars. What fraction of liquid would be condensed according to the PREOS (k_{ij}=0)?

Solution: Refer back to the same problem for an ideal solution for guess.

$L/F = 0.75 \Rightarrow x = \{0.1829,0.7053,0.1117\}$ and $y = \{0.3713,0.5624,0.0648\}$

						L/F= 0.75	L/F= 0.90	L/F= 0.867		
Co	*Tc*	*Pc*	ω	z_i	K_i	D_i	D_i	D_i	x_i	y_i
C3	369.8	42.49	0.152	0.23	1.729	-0.142	-0.1563	-.1528	.2097	.3625
iC4	408.1	36.48	0.177	0.67	0.832	0.118	0.1146	0.1153	.6853	.5700
nC4	425.2	37.97	.193	0.10	0.640	0.040	0.0373	0.0378	.1050	.0673
						0.016	-0.004	0.0002	1.000	.9998

For comparison, L/F = 0.87 (PR) vs. 0.75 (IS)

	Propane	Isobutane	n-Butane
K_i (PR)	1.727	0.833	0.641
K_i (IS)	2.03	0.80	0.58

Phase Envelope for PREOS

Use the PREOS(k_{ij}=0) to determine the phase envelope of nitrogen+methane at 150K. Plot P vs. x_{N2}, y_{N2} and compare the results from PREOS to the results from the "short-cut" result.

Solution: use the last guess as the initial guess for the next guess. Above 0.5 mole fraction, increment x_{N2} by 0.02 each time or you will not converge.