Example 7.1
Consider the ternary system: Acetone (1) / Acetonitrile (2) / Nitromethane (3) for which:

\[ \ln P^s_1 = 14.5463 - \frac{2940.46}{t + 237.22}, \ln P^s_2 = 14.5463 - \frac{2940.46}{t + 237.22}, \ln P^s_3 = 14.2043 - \frac{2972.64}{t + 209.00} \]

Calculate: (a) \( P, \{y_i\} \) for a temperature = 80\(^{o}\)C, \( x_1 = 0.3, x_2 = 0.3 \) (b) \( P, \{x_i\} \), for \( t = 70^{o}\)C, \( y_1 = 0.5, y_2 = 0.3 \).

(a) For 80\(^{o}\)C, \( P_1^s = 195.75, P_2^s = 97.84, P_3^s = 50.32 \) KPa. Thus:
\[ P = \sum x_i P^s_i = 108.3 KPa \]
Next:
\[ y_i = x_i P^s_i / P \]
Thus:
\[ y_1 = 0.54, y_2 = 0.27, y_3 = 0.19 \]

(b) For 70\(^{o}\)C, \( P_1^s = 144.77, P_2^s = 70.37, P_3^s = 43.80 \) KPa
\[ P = 1 / \sum y_i P^s_i = 81.4 KPa \]
Next:
\[ x_i = y_i P / P^s_i \]
Thus:
\[ x_1 = 0.28, x_2 = 0.34, x_3 = 0.38 \]

Example 7.2
A liquid mixture containing equimolar amounts of benzene (1) /toluene (2) and ethylbenzene (3) is flashed to conditions of \( T = 110^{o}\)C, \( P = 90 \) kPa, determine the equilibrium mole fractions \( \{x_i\} \) and \( \{y_i\} \) of the liquid and vapor phase formed and the molar fraction \( V \) of the vapor formed. Assume that Raoult’s law applies. \( \ln P^{sat}(Pa) = A - \frac{B}{t(K)} + C \)

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>13.8594</td>
<td>2773.78</td>
<td>-53.08</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>14.0045</td>
<td>3279.47</td>
<td>-59.95</td>
</tr>
<tr>
<td>Toluene</td>
<td>14.0098</td>
<td>3103.01</td>
<td>-53.36</td>
</tr>
</tbody>
</table>

At \( T = 383K \), the saturation vapour pressures are: \( P_1^s = 233.2; P_2^s = 99.1; P_3^s = 47.1kPa \)
Thus: \( K_1 = P_1^s / P = 2.6; \) similarly \( K_2 = 1.1; K_3 = 0.52 \)
For flash \[ \sum_{i=1}^{n} \frac{Z_i K_i}{1 + V(K_i - 1)} = 1 \]

Thus: \[ \frac{Z_1 K_1}{1 + V(K_1 - 1)} + \frac{Z_2 K_2}{1 + V(K_2 - 1)} + \frac{Z_3 K_3}{1 + V(K_3 - 1)} = 1 \] ..(1)

\[ Z_1 = Z_2 = Z_3 = 0.33 \]

On substituting the values of \( K_i \) and \( Z_i \) by solving eqn. (1) on obtains: \( V = 0.834 \)

**Example 7.3**

Methanol (1)-acetone (2) forms an azeotrope at 760 Torr with \( x_1 = 0.2, T = 55.7^\circ C \). Using van Laar model predict the bubble pressure for a system with for \( x_1 = 0.1 \) at 55.7\(^\circ\)C.

\[
\log_{10} P_1^a = 8.0897 - [1582.271/(t + 239.726)]; \log_{10} P_2^a = 7.1171 - [1210.595/(t + 229.664)]
\]

\[ P_i^a \text{ (torr); } t(\circ C) \]

At 55.7\(^\circ\)C \( P_1^a = 541.75 \text{Storr; } P_2^a = 745.5 \text{Storr} \)

We assume that the vapour phase is ideal. Hence the VL equation is given by:

\[ y_i P = x_i \gamma_i P_i^s \]

At the azeotropic condition: \( y_i = x_i \)

Hence,

\[ \gamma_i = P / P_i^s \]

Thus \( \gamma_1 = 1.4313, \ln \gamma_1 = 0.3607 \) and \( \gamma_2 = 1.0318, \ln \gamma_2 = 0.0137 \)

The Van Laar parameters are estimated next using the azeotrophic composition given by \( x_1 = 0.2 \) and \( x_2 = 0.8 \):

\[ A_{12} = \ln \gamma_1 \left(1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1}\right)^2 = 0.4786 \]

\[ A_{21} = \ln \gamma_2 \left(1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2}\right)^2 = 0.7878 \]

Thus \( \ln \gamma_1 = \frac{A_{12}}{1 + \frac{A_{12}x_1}{A_{21}x_2}}; \ln \gamma_2 = \frac{A_{21}}{1 + \frac{A_{21}x_2}{A_{12}x_1}} \)

For \( x_1 = 0.1, \gamma_1 = 1.5219, \gamma_2 = 1.0032 \)

\[ \therefore P = \sum x_i \gamma_i P_i^s = 757.62 \text{torr}, \gamma_i x_i P_i^s / P = 0.1067 \]

**Example 7.4**
For a binary, the activity coefficients are \( \ln \gamma_1 = A x_2 \) and \( \ln \gamma_2 = A x_1 \). Show that the system forms an azeotrope when \( A > \left| \ln \left( \frac{P_2^*}{P_1^*} \right) \right| \)

Again \( \gamma_1 = \frac{P}{P_1^*}, \gamma_2 = \frac{P}{P_2^*} \)

\[
\ln \gamma_1 = A x_2^2 = \ln \left( \frac{P}{P_1^*} \right); \ln \gamma_2 = A x_1^2 = \ln \left( \frac{P}{P_2^*} \right)
\]

\[
\therefore A(x_2^2 - x_1^2) = \ln \left( \frac{P_2^*}{P_1^*} \right)
\]

or \( A(x_2 - x_1) = A(1 - 2x_1) = \ln \left( \frac{P_2^*}{P_1^*} \right) \)

or \( x_1 = \frac{1}{2} \left[ 1 - \frac{1}{A} \ln \left( \frac{P_2^*}{P_1^*} \right) \right] \)

For azeotropy \( 0 < x_1 < 1 \)

If \( x_1 = 0 \), then \( A = \ln \left( \frac{P_2^*}{P_1^*} \right) \)

If \( x_1 = 1 \), then \( A = -\ln \left( \frac{P_2^*}{P_1^*} \right) \)

Thus for azeotropy to exist \( A > \left| \ln \left( \frac{P_2^*}{P_1^*} \right) \right| \)

**Example 7.5**

Estimate the vapour pressure of a substance “A” using PR-EoS, at \( T = 428^\circ K \). For the substance A: \( T_C = 569.4 \) K, \( P_C = 2.497 \) MPa, \( = 24.97 \) bar \( \omega = 0.398 \).

\( T_r = 0.7514 \)

At this temperature for starting the iteration, assume \( P^{\text{sat}} = 0.215 \) MPa

\( f_\omega = 0.37464 + 1.54226\omega - 0.26992 \omega^2 = 0.94570 \)

\( \alpha_{PR} = \left[ 1 + f_\omega \left( 1 - \sqrt{T_r} \right) \right]^2 = 1.2677 \)

\[
a = \frac{0.45724 R^2 T_C^2 \alpha_{PR}}{P_C} = \frac{0.45724 x \left( 8.314 \text{ Pa.m}^3 / \text{ mol}^\circ K \times 569.4 \right)^2 x1.2677}{24.97 \times 10^5} = 5.2024 \text{ Pa.m}^6/\text{mol}^2
\]

\[
b = \frac{0.07780 \ RT_C}{P_C} = \frac{0.07780 \times 8.314 \times 569.4}{24.97 \times 10^5} = 1.4750 \times 10^{-4} \text{ m}^3/\text{mol}
\]

\[
A = aP / (RT)^2 = \frac{5.2024 \times 0.215 \times 10^6}{(8.314 \times 428.0)^2} = 8.8398 \times 10^{-2}
\]

Assuming \( P = P^{\text{sat}} \).
\[ B = \frac{bP}{RT} = \frac{1.4750 \times 10^4 \times 0.215 \times 10^6}{8.314 \times 428} = 8.9151 \times 10^{-3} \]

\[ Z^3 + \alpha Z^2 + \beta Z + \gamma = 0 \]

\[ \alpha = -1 + B = -0.9911 \]

\[ \beta = A - 2B - 3B^2 = 7.0329 \times 10^{-2} \]

\[ \gamma = -AB + B^2 + B^3 = -7.0789 \times 10^{-4} \]

On solving \( Z_1 = 0.9151, \quad Z_2 = 1.2106 \times 10^{-2}, \quad Z_3 = 6.39 \times 10^{-2} \)

Thus \( Z^V = 0.9151, \quad Z^L = 1.2106 \times 10^{-2} \).

Now by PR-EoS: \[ \ln \phi = (Z - 1) - \ln (Z - B) - \frac{a}{2 \sqrt{2} bRT} \ln \left( \frac{Z + B(1 + \sqrt{2})}{Z + B(1 - \sqrt{2})} \right) \]

\[ \therefore \text{ Putting } Z = Z^L \]

\[ \ln \phi^V \phi^L = (1.2106 \times 10^{-2}) - \ln [1.2106 - 8.9151 \times 10^{-3}] \]

\[ = -0.0978 \Rightarrow \phi^V = 0.90 \Rightarrow f^L = \phi^L P = 0.19 \text{ MPa} \]

\[ -0.0821 \Rightarrow \phi^V = 0.9212 \]

or \( f^V = 0.1981 \)

\[ \Rightarrow \text{ If } f^V > f^L, \quad \text{ assumed value of } P (=P_{\text{sat}}) < \text{ actual } P_{\text{sat}} \]

\[ \Rightarrow \text{ If } f^L < f^V, \quad \text{ assumed value of } P (=P_{\text{sat}}) > \text{ actual } P_{\text{sat}} \]

\[ P_{\text{(revised)}} = P \frac{f^L}{f^V} \]

For the present case \( P_{\text{revised}} = 0.215 \times 0.195 \div 0.1981 = 0.2116 \text{ MPa} \)

Use revised ‘P’ to recalculate A, B, \{Z_i\}; thus:

\[ A = \frac{aP}{(RT)^2} = 8.6999 \times 10^{-2}; \quad B = \frac{bP}{RT} = 8.7742 \times 10^{-3} \]

\[ \therefore \alpha = -6.8568 \times 10^{-4}; \beta = 6.922 \times 10^{-2}; \gamma = -6.8568 \times 10^{-4} \]

Resolving \( f(z) = 0 \Rightarrow Z_1 = 0.9166; \quad Z_2 = 6.2907 \times 10^{-4}; \quad Z_3 = 1.1711 \times 10^{-2} \)

Hence new \( Z^V = 0.9166; \quad Z^L = 1.1711 \times 10^{-2} \)

Using \( Z = Z^V \) and \( Z = Z^L \) respectively

New \( \phi \phi^V = 0.9225 \Rightarrow f^V = (0.9225 \times 0.2116) = 0.1952 \text{ MPa} \)

Similarly \( \phi^L = 0.9224 \Rightarrow f^L \sim 0.1952 \text{ MPa} \)
Thus \( P_{\text{sat}} \approx 0.2116 \text{ MPa}\) (at 428\(^\circ\)K).

**Example 7.6**

A vapour mixture contains 20mol% methane (1), 30mol% ethane (2), and rest propane (3), at 30\(^\circ\)C. Determine the dew composition.

Assume \( P = 2.15 \text{ MPa}\)

\( \text{At 30}^\circ\text{C, and 2.15 MPa} \) read off the K factors from the charts.

\( K_1 = 8.1, \ K_2 = 1.82, \ K_3 = 0.62 \)

\[ x_1 = \frac{y_1}{K_1} = \frac{0.2}{8.1} = 0.0247 \]

\[ x_2 = \frac{y_2}{K_2} = \frac{0.3}{1.82} = 0.1648 \]

\[ x_3 = \frac{y_3}{K_3} = \frac{0.5}{0.62} = 0.8065 \]

\[ \sum x_i = 0.9960 \approx 1 \]

Hence dew pressure = 2.15 MPa. The dew composition therefore corresponds to the values of \( x_i \) computed above.

**Example 7.7**

For the system of methane (1) and butane (2) compute the bubble pressure for a liquid phase composition of \( x_1 = 0.2 \) at a temperature of 310K, using the PR-EOS.

\( P \text{ (guessed): } 40.8 \text{ bar} \)

\( y_1 \text{ (guessed)} = 0.85; \ y_2 = 0.15; \)

First consider calculation of the species fugacity coefficients for the liquid phase as \( T, \ P \) and \( x_1 (=0.2) \) are all know. For this one needs to solve for the cubic EOS with liquid phase compositions.

\( T = 310\text{K}, \ P = 40.8\text{bar} \)

For each species the following estimates are made:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Methane (1)</th>
<th>Butane (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_{\omega} )</td>
<td>( 3.9310 \times 10^{-3} )</td>
<td>( 6.7229 \times 10^{-3} )</td>
</tr>
</tbody>
</table>
With $x_1 = 0.2$, it follows that

$$a_m = x_1^2a_1 + 2x_1x_2(a_1a_2)^{1/2} + x_2^2a_2 = 1.3592 \text{ Pa m}^{-6} / \text{mol}$$

$$b_m = x_1b_1 + x_2b_2 = 0.000063 \text{ m}^3 / \text{mol}$$

$$A_m = \frac{a_mP}{RT^2} = 0.8304$$

$$B_m = \frac{b_mP}{RT} = 0.10$$

With the above values of $A$ and $B$ solve the cubic PR-EOS. The roots are as:

$Z_1 = 0.1471$

$Z_2 = 0.3764 + 0.5899i$

$Z_3 = 0.3764 - 0.5899i$

The feasible root for the liquid phase is: $Z_L = 0.1471$

Now using the generalized expression for species fugacity coefficients for PR-EOS:

$$\ln \hat{\phi}_i = \frac{b_i}{b_m}(Z - 1) - \ln(Z - B) + \frac{a_m}{2\sqrt{2b_mRT}} \left[ \frac{b_i}{b_m} - 2\sqrt{\frac{a_i}{a_m}} \right] \ln \left[ \frac{Z + B(1 + \sqrt{2})}{Z + B(1 - \sqrt{2})} \right]$$

Using: $Z = Z_L = 0.1471$; $B = B_m$

$$\ln \hat{\phi}_i = \frac{b_i}{b_m}(Z_L - 1) - \ln(Z_L - B_m) + \frac{a_m}{2\sqrt{2b_mRT}} \left[ \frac{b_i}{b_m} - 2\sqrt{\frac{a_i}{a_m}} \right] \ln \left[ \frac{Z_L + B_m(1 + \sqrt{2})}{Z_L + B_m(1 - \sqrt{2})} \right]$$

whence: $\hat{\phi}_i^L = 4.0271$

Similarly: $\hat{\phi}_i^L = 0.0932$

Next compute the fugacity coefficients for the vapour phase. The calculations are the same as above except that $x_i$ is replaced with $y_i$. (Note that the pure component properties remain the same as in Table 1, since the $T$ and $R$ are the same, i.e, 310K and 40.8bar, respectively.

With $y_1 = 0.85$, it follows that

$$a_m = y_1^2a_1 + 2y_1y_2(a_1a_2)^{1/2} + y_2^2a_2 = 0.3323 \text{ Pa m}^{-6} / \text{mol}$$

$$b_m = y_1b_1 + y_2b_2 = 0.000033 \text{ m}^3 / \text{mol}$$

$$A_m = \frac{a_mP}{RT^2} = 0.2030$$

$$B_m = \frac{b_mP}{RT} = 0.0528$$
With the above values of A and B solve the cubic PR-EOS. The roots are as:

\[ Z_1 = 0.8537 \]
\[ Z_2 = 0.0467 + 0.0833i \]
\[ Z_3 = 0.0467 - 0.0833i \]

The feasible root for the liquid phase is: \( Z^L = 0.8537 \)

Now using the generalized expression for species fugacity coefficients for PR-EOS:

\[
\ln \hat{\phi}_i = \frac{b_i}{b_m} (Z - 1) - \ln(Z - B) + \frac{a_m}{2\sqrt{2b_mRT}} \left( \frac{b_i}{b_m} - 2 \right) \ln \left( \frac{Z + B(1 + \sqrt{2})}{Z + B(1 - \sqrt{2})} \right)
\]

Using: \( Z = Z^L = 0.8537; \ B = B_m \sqrt{2} \)

\[
\ln \hat{\phi}_1 = \frac{b_1}{b_m} (Z^L - 1) - \ln(Z^L - B_m) + \frac{a_m}{2\sqrt{2b_mRT}} \left( \frac{b_1}{b_m} - 2 \right) \ln \left( \frac{Z^L + B_m(1 + \sqrt{2})}{Z^L + B_m(1 - \sqrt{2})} \right)
\]

whence: \( \hat{\phi}_1^L = 0.9399 \)

Similarly: \( \hat{\phi}_2^L = 0.5184 \)

Therefore:

\[
K_1 = \frac{y_1}{x_1} = \frac{\hat{\phi}_1^L}{\hat{\phi}_1^V} = 4.0271
\]

\[
y_1 = K_1 x_1 = 0.8569
\]

\[
K_2 = \frac{y_2}{x_2} = \frac{\hat{\phi}_2^L}{\hat{\phi}_2^V} = 0.0932
\]

\[
y_2 = K_2 x_2 = 0.1438
\]

Thus: \( \sum y_i = 1.0007 \)

Therefore we may terminate the iteration at this point.

Bubble Pressure = 40.8bar
\[ y_1 = 0.8569 \]

**Example 7.8**

A concentrated binary solution containing mostly species 2 (but \( x_2 \neq 1 \)) is in equilibrium with a vapor phase containing both species 1 and 2. The pressure of this two-phase system is 1 bar; the temperature is 298.0K. Determine from the following data good estimates of \( x_1 \) and \( y_1 \).

\( H_1 = 200 \text{ bar}, \ p_{2\text{sat}} = 0.1 \text{ bar}. \)

\( H_1 = 200 \text{ bar}, \ P_\text{2}^s = 0.1 \text{ bar}, \ P = 1 \text{ bar} \)
Assume that vapor phase is ideal at $P = 1$ bar. Assume Lewis - Randall rule applies to concentrated species and Henry’s law to dilute species then:

\[ y_1 P = H_1 x_1 \quad \text{And} \quad y_2 P = x_2 P_2^s \]

Now \[ P = (y_1 + y_2)P = y_1 P + y_2 P = H_1 x_1 + x_2 P_2^s \]

Or \[ P = H_1 x_1 + (1 - x_1)P_2^s \] → Solving gives, \( x_1 = 4.5 \times 10^{-3} \) and \( y_1 = 0.9 \)