Example 7.1

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

$$\ln P_1^S = 14.5463 - \frac{2940.46}{t+237.22}; \quad \ln P_2^S = 14.5463 - \frac{2940.46}{t+237.22}; \quad \ln P_3^S = 14.2043 - \frac{2972.64}{t+209.00}$$

$P_i^S (KPa); t(^0C).$

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

(a) For 80°C, $P_1{}^S$ = 195.75, $P_2{}^S$ = 97.84, $P_3{}^S$ = 50.32 KPa. Thus:

$$P = \sum x_i P_i^S = 108.3 KPa$$

Next:

$$y_i = x_i P_i^S / P$$

Thus:

$$y_1 = 0.54, \ y_2 = 0.27, \ y_3 = 0.19$$

(b) For 70°C, $P_1{}^S$ = 144.77, $P_2{}^S$ = 70.37, $P_3{}^S$ = 43.80 KPa

$$P = 1/\sum y_k / P_k^S = 81.4 \text{ KPa}$$

Next:

$$x_i = y_i P / P_i^S$$

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°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. $\ln P^{sat}(Pa) = A - \dfrac{B}{t(^0K)+C}$

	A	B	C
Benzene	13.8594	2773.78	-53.08
Ethylbenzene	14.0045	3279.47	-59.95
Toluene	14.0098	3103.01	-53.36

At T = 383K, the saturation vapour pressures are: $P_1^S = 233.2; \ P_2^S = 99.1; \ P_3^S = 47.1 kPa$

Thus: $K_1 = P_1^S / P = 2.6$; similarly $K_2 = 1.1; \ K_3 = 0.52$

For flash $\sum_{i=1}^{n} \dfrac{Z_i K_i}{1 + V(K_i - 1)} = 1$

Thus: $\dfrac{Z_1 K_1}{1 + V(K_1 - 1)} + \dfrac{Z_2 K_2}{1 + V(K_2 - 1)} + \dfrac{Z_3 K_3}{1 + V(K_3 - 1)} = 1$ ..(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°C. Using van Laar model predict the bubble pressure for a system with for $x_1 = 0.1$ at 55.7°C.

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

$P_i^s (torr); t(^0C)$

At 55.7°C $P_1^s = 541.75 torr; P_2^s = 745.5 torr$

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 azeotropic composition given by $x_1 = 0.2$ and $x_2 = 0.8$:

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

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

Thus $\ln \gamma_1 = \dfrac{A_{12}}{\left(1 + \dfrac{A_{12} x_1}{A_{21} x_2} \right)^2}; \ln \gamma_2 = \dfrac{A_{21}}{\left(1 + \dfrac{A_{21} x_2}{A_{12} x_1} \right)^2}$

For $x_1 = 0.1$, $\gamma_1 = 1.5219$, $\gamma_2 = 1.0032$

$\therefore P = \sum x_i \gamma_i P_i^s = 757.62$ torr, $y_1 = \gamma_1 x_1 P_1^s / P = 0.1067$

Example 7.4

For a binary, the activity coefficients are $\ln \gamma_1 = Ax_2^2$ and $\ln \gamma_2 = Ax_1^2$. Show that the system forms an azeotrope when $A > \left|\ln\left(P_2^s / P_1^s\right)\right|$

Again $\gamma_1 = P/P_1^s, \gamma_2 = P/P_2^s$

$\quad \ln \gamma_1 = Ax_2^2 = P/P_1^s ; \ln \gamma_2 = Ax_1^2 = P/P_2^s$

$\quad \therefore A\left(x_2^2 - x_1^2\right) = \ln\left(P_2^s/P_1^s\right)$

$\quad$ or $A\left(x_2 - x_1\right) = A(1 - 2x_1) = \ln\left(P_2^s/P_1^s\right)$

$\quad$ or $x_1 = \dfrac{1}{2}\left[1 - \dfrac{1}{A}\ln\left(P_2^s/P_1^s\right)\right]$

For azeotropy $0 < x_1 < 1$

If $x_1 = 0$, then $A = \ln\left(P_2^s/P_1^s\right)$

If $x_1 = 1$, then $A = -\ln\left(P_2^s/P_1^s\right)$

Thus for azeotropy to exist $A > \left|\ln P_2^s/P_1^s\right|$

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 $P^{sat} = 0.215$ MPa

$f_\omega = 0.37464 + 1.54226\omega - 0.26992\,\omega^2 = 0.94570$

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

$a = \dfrac{0.45724R^2T_C^2\alpha_{PR}}{P_C} = \dfrac{0.45724 \times \left(8.314\ Pa.m^3 / mol^{\circ}K \times 569.4\right)^2 \times 1.2677}{24.97 \times 10^5}$

$\qquad\qquad = 5.2024\ Pa.m^6/mol^2$

$b = \dfrac{0.07780\ RT_C}{P_C} = \dfrac{0.07780 \times 8.314 \times 569.4}{24.97 \times 10^5} = 1.4750 \times 10^{-4}\ m^3/mol$

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

Assuming $P = P^{sat}$:

$$B = bP/RT = \frac{1.4750 \times 10^{-4} \times 0.215 \times 10^{6}}{8.314 \times 428} = 8.9151 \times 10^{-3}$$

$$Z^{3} + \alpha Z^{2} + \beta Z + \gamma\gamma = 0$$

$\alpha = -1+B = -0.9911$

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

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

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

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

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

$\therefore\therefore$ Putting $Z = Z^{L}$

$\ln\phi^{L}\phi^{L} = (1.2106 \times 10^{-2}) -1-\ln[1.2106 - 8.9151 \times 10^{-3}]$

$$-\frac{5.2024}{2\sqrt{2} \times 1.475 \times 10^{-4} \times 8.314 \times 428} \times \ln\left\{\frac{0.9151 + 8.9151 \times 10^{-3}(1+\sqrt{2})}{0.9151 + 8.9151 \times 10^{-3}(1+\sqrt{2})}\right\}$$

$$= -0.0978 \Rightarrow \phi^{L} = 0.90 \Rightarrow f^{L} = \phi^{L}P = 0.19 MPa = -0.0978 \Rightarrow \phi^{L} = 0.90 \Rightarrow f^{L} = \phi^{L}P =$$

0.19 MPa

Similarly putting $Z = Z^{V}$ gives $\ln\phi^{V} = -0.0821 \Rightarrow\Rightarrow \phi^{V} = 0.9212$

or $f^{V} = 0.1981$

$\rightarrow\rightarrow$ If $f^{L} > f^{V}$, $\qquad$ assumed value of P $(=P^{sat}) <$ actual P^{sat}

$\rightarrow$ If $f^{L} < f^{V}$, assumed value of P $(=P^{sat)} >$ actual P_{sat}

$$P_{(revised)} = P\,\frac{f^{L}}{f^{V}}$$

For the present case $P_{revised} = 0.215 \times \dfrac{0.195}{0.1981} = 0.2116$ MPa

Use revised 'P' to recalculate A, B, $\{Z_i\}$; thus:

$A = aP/(RT)^{2} = 8.6999 \times 10^{-2}$; $B = bP/RT = 8.7742 \times 10^{-3}$

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

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

Hence new $Z^{V} = 0.9166$; $\qquad Z^{L} = 1.1711 \times 10^{-2}$

Using $Z = Z^{V}$ and $Z = Z^{L}$ respectively

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

Similarly $\phi^{L} = 0.9224 \Rightarrow f^{L} \sim 0.1952$ MPa

Thus $P^{sat} \sim 0.2116$ MPa   (at 428°K).

Example 7.6

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

Assume $P = 2.15 \ MPa$

$At \ 30°C, and \ 2.15 \ MPa$ read off the K factors from the charts.

$K_1 = 8.1, \ K_2 = 1.82, \ K_3 = 0.62$

$$x_1 = \frac{y_1}{K_1} = \frac{0.2}{8.1} = 0.0247$$

$$x_2 = \frac{y_2}{K_2} = \frac{0.3}{1.82} = 0.1648$$

$$x_3 = \frac{y_3}{K_3} = \frac{0.5}{0.62} = 0.8065$$

$$\sum x_i = 0.9960 \sim 1$$

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 (guessed): 40.8 bar

y_1 (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 = 310K, P = 40.8bar

For each species the following estimates are made:

Table 1

Parameter	Methane (1)	Butane (2)
f_ω	3.9310 x 10^{-3}	6.7229 x 10^{-3}

a $(Pa.m^{-6}/mol^2)$	0.198207	1.811717
b (m^3/mol)	0.000027	0.000072

With $x_1 = 0.2$, it follows that

$$a_m = x_1^2 a_1 + 2x_1 x_2 (a_1 a_2)^{1/2} + x_2^2 a_2 = 1.3592\ Pa.m^{-6} / mo\ \ell$$

$$b_m = x_1 b_1 + x_2 b_2 = 0.000063\ m^3 / mol$$

$$A_m = \frac{a_m P}{R^2 T^2} = 0.8304$$

$$B_m = \frac{b_m P}{RT} = 0.10$$

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:

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

Using: $Z = Z^L = 0.1471$; $B = B_m$

$$\ln \hat{\phi}_1 = \frac{b_1}{b_m}(Z^L - 1) - \ln(Z^L - B_m) + \frac{a_m}{2\sqrt{2} b_m RT}\left[\frac{b_1}{b_m} - 2\sqrt{\frac{a_1}{a_m}}\right] \ln\left[\frac{Z^L + B_m(1+\sqrt{2})}{Z^L + B_m(1-\sqrt{2})}\right]$$

whence: $\hat{\phi}_1^L = 4.0271$

Similarly: $\hat{\phi}_2^L = 0.0932$

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

$$a_m = y_1^2 a_1 + 2y_1 y_2 (a_1 a_2)^{1/2} + y_2^2 a_2 = 0.3323\ Pa.m^{-6} / mo\ \ell$$

$$b_m = y_1 b_1 + y_2 b_2 = 0.000033\ m^3 / mol$$

$$A_m = \frac{a_m P}{R^2 T^2} = 0.2030$$

$$B_m = \frac{b_m P}{RT} = 0.0528$$

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: $Z^V = 0.8537$

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

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

Using: $Z = Z^V = 0.8537$; $B = B_m$

$$\ln \hat{\phi}_1 = \frac{b_1}{b_m}(Z^V-1) - \ln(Z^V-B_m) + \frac{a_m}{2\sqrt{2}b_m RT}\left[\frac{b_1}{b_m} - 2\sqrt{\frac{a_1}{a_m}}\right]\ln\left[\frac{Z^V+B_m(1+\sqrt{2})}{Z^V+B_m(1-\sqrt{2})}\right]$$

whence: $\hat{\phi}_1^V = 0.9399$

Similarly: $\hat{\phi}_2^V = 0.5184$

Therefore:

$$K_1 = \frac{y_1}{x_1} = \frac{\hat{\phi}_1^L}{\hat{\phi}_1^V} = \frac{4.0271}{0.9399} = 4.2846$$

$$y_1 = K_1 x_1 = 0.8569$$

$$K_2 = \frac{y_2}{x_2} = \frac{\hat{\phi}_2^L}{\hat{\phi}_2^V} = \frac{0.0932}{0.5184} = 0.1798$$

$$y_2 = K_2 x_2 = 0.1438$$

Thus : $\sum_i y_i = 1.0007$

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.

$H_1 = 200$ bar; $P_2^{sat} = 0.10$ bar.

$H_1 = 200$ bar, $P_2^s = 0.1$ bar, $P = 1$ 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:

$y_1 P = H_1 x_1$ And $y_2 P = x_2 P_2^s$

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 $y_1 = 0.9$