## Example 10.3

For the system methanol(1)/methyl acetate(2), the following equations provide a reasonable correlation for the activity coefficients:

$$\ln \gamma_1 = Ax_2^2 \qquad \ln \gamma_2 = Ax_1^2 \qquad \text{where} \qquad A = 2.771 - 0.005\,23T$$

In addition, the following Antoine equations provide vapor pressures:

$$\ln P_1^{sat} = 16.591\,58 - \frac{3643.31}{T - 33.424} \qquad \ln P_2^{sat} = 14.253\,26 - \frac{2665.54}{T - 53.424}$$

where $T$ is in kelvins and the vapor pressures are in kPa. Assuming the validity of Eq. (10.5), calculate:

(a) $P$ and $\{y_i\}$, for $T$ = 318.15 K (45°C) and $x_1$ = 0.25.
(b) $P$ and $\{x_i\}$, for $T$ = 318.15 K (45°C) and $y_1$ = 0.60.
(c) $T$ and $\{y_i\}$, for $P$ = 101.33 kPa and $x_1$ = 0.85.
(d) $T$ and $\{x_i\}$, for $P$ = 101.33 kPa and $y_1$ = 0.40.
(e) The azeotropic pressure, and the azeotropic composition, for $T$ = 318.15 K (45°C).

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(a) For $T = 318.15$ K and $x_1 = 0.25$ & $x_2 = 0.75$
Find $y_i$ & $P$

$\Rightarrow$ from the above equations:

$P_1^{sat} = 44.51$ kPa & $P_2^{sat} = 65.64$ kPa

$A = 1.107$, $\gamma_1 = 1.864$ & $\gamma_2 = 1.072$

$$y_i P = x_i \gamma_i P_i^{sat} \qquad (i = 1, 2, \cdots, N)$$

add the above equation for all components

$$\underbrace{\cancel{(y_1 + y_2)}}_{1} P = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat}$$

$\Rightarrow P = 73.5$ kPa

$$y_1 = \frac{x_1 \gamma_1 P_1^{sat}}{P} = 0.282 \Rightarrow y_2 = 0.718$$

(b) $T = 318.15\ K$ & $y_1 = 0.6$

Find $P$ and $x_i$

since $T$ is known $\Rightarrow P_1^{sat}$, $P_2^{sat}$ and $A$ can be calculated:

$P_1^{sat} = 44.51$ kPa

$P_2^{sat} = 65.64$ kPa

$A = 1.107$

Modified Raoult's law:

$$y_i P = x_i \gamma_i P_i^{sat} \qquad (i = 1, 2, \ldots, N)$$

since $x_i$ is unknown $\Rightarrow \sum_i x_i = 1$

$$\Rightarrow 1 = \sum_i \frac{y_i P}{\gamma_i P_i^{sat}}$$

$$= P \sum_i \frac{y_i}{\gamma_i P_i^{sat}}$$

$$\Rightarrow P = \frac{1}{\sum_i \frac{y_i}{\gamma_i P_i^{sat}}} = \frac{1}{\frac{y_1}{\gamma_1 P_1^{sat}} + \frac{y_2}{\gamma_2 P_2^{sat}}}$$

$$\gamma_1 = \exp\left[A\, x_2^2\right] = \exp\left[A (1-x_1)^2\right]$$

$$\gamma_2 = \exp\left[A\, x_1^2\right]$$

$$\Rightarrow P = \frac{1}{\dfrac{y_1}{\exp\left[A(1-x_1)^2\right] P_1^{sat}} + \dfrac{y_2}{\exp\left[A\, x_1^2\right] P_2^{sat}}} \quad (1)$$

we need one more equation

$$y_1 P = x_1 \gamma_1 P_1^{sat} \quad - - - - - - \quad (2)$$

substitute all known variables in (1) & (2)

$$P = \frac{1}{\dfrac{0.6}{\exp\left[1.107\,(1-x_1)^2\right] 44.51} + \dfrac{0.4}{\exp\left[1.107\, x_1^2\right] 65.64}}$$

$$0.6\, P = x_1 \exp\left[1.107\,(1-x_1)^2\right]\; 44.51$$

simplify :

$$P = \frac{1}{\dfrac{1.348 * 10^{-2}}{\exp\left[1.107(1-x_1)^2\right]} + \dfrac{6.094 * 10^{-3}}{\exp\left[1.107\, x_1^2\right]}} \quad (1)$$

$$x_1 \exp\left[1.107(1-x_1)^2\right] = 1.348 * 10^{-2} \; P \quad --- (2)$$

Here we have two coupled equations with two unknowns $x_1$ & $P$.

solution procedure:

(a) Guess $x_1$ and substitute in (1) to calculate $P$.

(b) substitute calculated value of $P$ in (2) and calculate $x_1$ (by trail and error).

(c) check is $x_{1\,calculated} \overset{?}{=} x_{1\,guess}$

if yes stop. If not $x_{1\,guess} = x_{1\,calculated}$ and continue

## iteration #1

$X_{1\,guess} = 0.5$ substitute in 1

$\Rightarrow P = 67.377$ kPa substitute in 2

$\Rightarrow x_1 \exp\left[1.107(1-x_1^2)\right] = 0.908$

$\Rightarrow x_{1\,calculated}$ (by trail and error) $= 0.900$

$X_{1\,calculated} \neq X_{1\,guess}$

| Iteration # | $X_{1\,guess}$ | P(kpa) | $X_{1\,calculated}$ |
|---|---|---|---|
| 1 | 0.5 | 67.377 | 0.900 |
| 2 | 0.900 | 63.221 | 0.823 |
| 3 | 0.823 | 62.894 | 0.817 |
| 4 | 0.817 | 62.893 | 0.817 |

$$\Rightarrow \quad x_{1\,calculated} \cong x_{1\,guess}$$

note this is done with three significant digits only.

$x_1 = 0.817$ , $P = 62.893$ kPa

(c) $P = 101.33$ KPa , $x_1 = 0.85$

Find $T$ and $y_1$

$$y_i P = x_i \gamma_i P_i^{sat}$$

$$\sum_i y_i = 1$$

$$\Rightarrow \quad P = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat} \quad --- \quad (1)$$

$$y_1 = \frac{x_1 \gamma_1 P_1^{sat}}{P} \quad --- \quad (2)$$

two equations with two unknowns

$T$ & $y_1$

substitute all known variables in ⑧

① & ②

$$101.33 = 0.85 \exp\left[(2.771 - 0.00523T)(0.15)^2\right] * \exp\left[16.59158 - \frac{3643.31}{T - 33.424}\right]$$

$$+ 0.15 \exp\left[(2.771 - 0.00523T)(0.85)^2\right] * \exp\left[14.25326 - \frac{2665.54}{T - 53.424}\right] \quad \text{---} ①$$

$$y_1 = \frac{0.85 \exp\left[2.771 - 0.00523T\right] * \dfrac{\exp\left[16.59158 - \dfrac{3643.31}{T - 33.424}\right]}{1}}{101.33} \quad ②$$

Two un-coupled equations with two unknowns $T$ and $y_1$

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solve for T from 1 by trail and error the substitute in 2 to calculate $y_1$.

$T = 331.2\ K$

$y_1 = 0.670$

(e) $T = 318.15\,K$

$$\Rightarrow P_1^{sat} = 44.51 \text{ kPa}, \quad P_2^{sat} = 65.64 \text{ kPa}$$

$$A = 1.107$$

$$\gamma_1 = \exp\left[\overset{1.107}{A}(1-x_1)^2\right], \quad \gamma_2 = \exp\left[1.107\, x_1^2\right]$$

modified Raoult's Law:

$$y_1 P = x_1 \gamma_1 P_1^{sat} \quad \text{---} \; 1$$

$$y_2 P = x_2 \gamma_2 P_2^{sat} \quad \text{---} \; 2$$

substitute values:

$$y_1 P = x_1 \exp\left[1.107(1-x_1)^2\right] 44.51$$

$$(1-y_1) P = (1-x_1) \exp\left[1.107\, x_1^2\right] 65.64$$

at the azeotrop $y_1 = x_1$

$$\Rightarrow \begin{cases} \cancel{x_1} P = \cancel{x_1} \exp\left[1.107(1-x_1)^2\right] 44.51 & \text{---} \; 1 \\ \cancel{(1-x_1)} P = \cancel{(1-x_1)} \exp\left[1.107\, x_1^2\right] 65.64 & \text{---} \; 2 \end{cases}$$

$$\Rightarrow \exp\left[1.107(1-x_1)^2\right] 44.51 = \exp\left[1.107\, x_1^2\right] 65.6$$

Rearrange :

$$\frac{44.51}{65.64} \exp\left[1.107\,(1-x_1)^2\right] - \exp\left[1.107\,x_1^2\right] =$$

by trail and error $x_1 \approx 0.325$

substitute in (1)

$$P = \exp\left[1.107\,(1-0.325)^2\right] 44.51$$

$$\Rightarrow P = 73.76 \text{ KPa}$$

also $y_1 = x_1 = 0.325$