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:

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

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

⇒ from the above equations:

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

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

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

add the above equation for all components

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

$$\Rightarrow P = 73.5 \text{ kPa}$$

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

(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:

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

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

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

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

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

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

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

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

we need one more equation

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

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

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

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

simplify:

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

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

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.

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

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

Find T and y_1

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

$\sum_i y_i = 1$

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

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

two equations with two unknowns

T & y_1

substitute all known variables in

1 & 2

$$101.33 = 0.85 \exp\left[(2.771 - 0.00523T)(0.15)^2\right] *$$

$$\exp\left[16.59158 - \frac{3643.31}{T - 33.424}\right]$$

$$+ 0.15 \exp\left[(2.771 - 0.00523T)(0.85)^2\right] *$$

$$\exp\left[14.25326 - \frac{2665.54}{T - 53.424}\right] \text{---} (1)$$

$$y_1 = \frac{0.85 \exp\left[2.771 - 0.00523T\right] \quad *}{101.33}$$

$$\frac{\exp\left[16.59158 - \dfrac{3643.31}{T - 33.424}\right]}{1} \quad (2)$$

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.

$T = 331.2\ K$

$y_1 = 0.670$