Exercise 9

Problem 1: Using the 1-parameter margules equation on a single experimental data point

A single vapor–liquid equilibrium point for the water (1) 1 ethanol (2) system is experimentally measured at 30°C. The experiment provides the following information:

$x_1 = 0.30$, $y_1 = 0.23$, and P = 10.1 kPa. Use this information to estimate the system pressure and vapor-phase mole fraction when $x_1 = 0.8$.

Given simplest model for real solutions known as the 1-parameter Margules equation:

$$\frac{G^E}{RT} = Ax_1x_2$$

where this relationship is general and not based on a model

$$\frac{G^E}{RT} = x_1 \ln[\gamma_1] + x_2 \ln[\gamma_2]$$

$$\ln[\gamma_i] : \textit{partial molar property of the excess Gibbs free energy}$$

Saturation pressure for the components given:

$$P_{1,sat} = 4.20\ kPa$$

$$P_{2,sat} = 10.42\ kPa$$

Activity coefficient expressions for 1 parameter Margules equation:

$$\ln \gamma_1 = A\, x_2^2$$

$$\ln \gamma_2 = A\, x_1^2$$

(I'm using the hint sheet here)

Using the modified Raoult's law:

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

$$\Rightarrow \gamma_i = \frac{y_i P}{x_i \cdot P_i^{sat}} \quad (1)$$

For the given data, $x_1 = 0{,}30$, $y_1 = 0{,}23$ and $P = 10{,}1$ kPa

$P_1^{sat} = 4{,}20$ kPa

$P_2^{sat} = 10{,}42$ kPa

We can easily calculate $x_2 = 0{,}7$ and $y_2 = 0{,}77$ $(x_2 = 1 - x_1)$

(1) $$\gamma_1 = \frac{0{,}23 \cdot 10{,}1\ \cancel{kPa}}{0{,}30 \cdot 4{,}2\ \cancel{kPa}} = 1{,}8437$$

$$\gamma_2 = \frac{0{,}77 \cdot 10{,}1\ \cancel{kPa}}{0{,}7 \cdot 10{,}42\ \cancel{kPa}} = 1{,}0662$$

We have to expressions for $\frac{G^E}{RT}$

$$\Rightarrow \quad A x_1 x_2 = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

$$\Rightarrow \quad A = \frac{\ln \gamma_1}{x_2} + \frac{\ln \gamma_2}{x_1} \quad (2)$$

$$(2) \quad A = \frac{\ln 1{,}8437}{0{,}70} + \frac{\ln 1{,}0662}{0{,}30}$$

$$\underline{A = 1{,}0877}$$

For $x_1 = 0{,}8$, $x_2 = 0{,}2$. Using $\ln(\gamma_1) = A x_2^2, \quad \ln(\gamma_2) = A x_1^2$

$$\Rightarrow \gamma_1 = \exp(A \cdot x_2^2), \quad \gamma_2 = \exp(A \cdot x_1^2)$$

We get: $\gamma_1 = 1{,}0445$, $\gamma_2 = 2{,}0060$

Rearranging the modified Raoult's law gives:

$$P = \frac{x_i \gamma_i P_i^{sat}}{y_i}, \quad \text{using } y_2 = 1 - y_1 \text{ gives:}$$

$$P = \frac{x_1 \gamma_1 P_1^{sat}}{y_1} = \frac{x_2 \gamma_2 P_2^{sat}}{1 - y_1} \qquad y_i P = x_i \gamma_i P_i^{sat}$$

$$(1 - y_1) x_1 \gamma_1 P_1^{sat} = y_1 x_2 \gamma_2 P_2^{sat}$$

$$x_1 \gamma_1 P_1^{sat} = y_1 (x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat})$$

$$y_1 = \frac{x_1 \gamma_1 P_1^{sat}}{x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat}}$$

Comparing to

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

We get that $P = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat}$

$= 0{,}8 \cdot 1{,}0445 \cdot 4{,}20\text{ kPa} + 0{,}2 \cdot 2{,}0060 \cdot 10{,}42\text{ kPa}$

$\boxed{P = 7{,}69\text{ kPa}}$

Then, using: $y_1 = \dfrac{x_1 \gamma_1 P_1^{sat}}{P}$

$$y_1 = \frac{0{,}8 \cdot 1{,}0445 \cdot 4{,}20\ \cancel{\text{kPa}}}{7{,}69\ \cancel{\text{kPa}}}$$

$\boxed{y_1 = 0{,}456}$

Problem 2:

You are interested in finding the pressure at which the first bubble of vapor will form from a liquid mixture of ethanol (1) and benzene (2) (49 % by mole ethanol) at 313 K. The Margules parameters for this mixture are A_{12} = 2.173 and A_{21} = 1.539, while the Wilson parameters for this mixture are $\frac{a_{12}}{R}$ = 653.13 K and $\frac{a_{21}}{R}$ = 66.16 K. Find the pressure and vapor-phase composition three ways:

a) Using the 2-parameter Margules equation
b) Using the Wilson equation
c) Using ideal solution

Given:

a) 2-parameter Margules equation:

$$\frac{G^E}{RT} = x_1 x_2 (A_{21} x_1 + A_{12} x_2)$$

where

$$\ln[\gamma_1] = x_2^2 (A_{12} + 2[A_{21} - A_{12}] x_1)$$

$$\ln[\gamma_2] = x_1^2 (A_{21} + 2[A_{12} - A_{21}] x_2)$$

b) Wilson equation

$$\frac{G^E}{RT} = -x_1 ln(x_1 + \Lambda_{12}\, x_2) - x_2 ln(x_2 + \Lambda_{21}\, x_1)$$

The activity coefficients for this model are given using the same approach as before:

$$\ln[\gamma_1] = -ln(x_1 + \Lambda_{12}\, x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}\, x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}\, x_1}\right)$$

$$\ln[\gamma_2] = -ln(x_2 + \Lambda_{21}\, x_1) - x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}\, x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}\, x_1}\right)$$

The temperature dependence of the parameters Λ_{12} and Λ_{21} is given as:

$$\Lambda_{12} = \frac{\underline{V}_2}{\underline{V}_1} exp\left(\frac{-a_{12}}{RT}\right)$$

$$\Lambda_{21} = \frac{\underline{V}_1}{\underline{V}_2} exp\left(\frac{-a_{21}}{RT}\right)$$

$\underline{V}$: liquid molar volume of the pure component at the mixture temperature where:

$\underline{V}_1$ (ethanol) : 58.68 cm³/mol

$\underline{V}_2$ (benzene): 89.41 cm³/mol

a_{12}: composition independent parameters that describe how the interactions between the unlike components differ from the like components

Also given:

$$P_{1,sat} = 134.95\ mm\ Hg$$

$$P_{2,sat} = 182.79\ mm\ Hg$$

Bubble point ⇒ approximately only liquid

$x_1 = 0{,}49$ and $x_2 = 0{,}51$

a)

Using the given equations

$\gamma_1 = \exp\left(0{,}51^2 (2{,}173 + 2[1{,}539 - 2{,}173]\, 0{,}49)\right)$

$\underline{\gamma_1 = 1{,}497}$

$\gamma_2 = \exp\left(0{,}49^2 (1{,}539 + 2[2{,}173 - 1{,}539]\, 0{,}49)\right)$

$\underline{\gamma_2 = 1{,}680}$

Using the expression found in the previous question

$P = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat}$

$P = 0{,}49 \cdot 1{,}497 \cdot 134{,}95 + 0{,}51 \cdot 1{,}680 \cdot 182{,}79$

$\boxed{P = 255{,}6\text{ mmHg}}$ ← Why is this not equal to the answer in the numerical solution?

Then, using the modified Raoult's law

$$y_1 = \frac{x_1 \gamma_1 P_1^{sat}}{P} = \frac{0{,}49 \cdot 1{,}497 \cdot 134{,}95}{255{,}6}$$

$\boxed{y_1 = 0{,}387}$

b) At T=313

$$\Lambda_{12} = \frac{V_2}{V_1} \exp\left(-\frac{\alpha_{12}}{RT}\right) = \frac{89{,}41}{58{,}68} \exp\left(-\frac{653{,}13\,K}{313\,K}\right)$$

$\Lambda_{12} = 0{,}1891$

$$\Lambda_{21} = \frac{V_1}{V_2} \exp\left(-\frac{\alpha_{21}}{RT}\right) = \frac{58{,}68}{89{,}41} \cdot \exp\left(-\frac{66{,}16\,K}{313\,K}\right)$$

$\Lambda_{21} = 0{,}5313$

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2+\Lambda_{21}x_1}\right)$$
$$= -\ln(0{,}49 + 0{,}1891 \cdot 0{,}51) + 0{,}51\left(\frac{0{,}1891}{0{,}49+0{,}1891\cdot 0{,}51} - \frac{0{,}5313}{0{,}51+0{,}5313\cdot 0{,}49}\right)$$
$$= 0{,}3464$$

$\Rightarrow \underline{\gamma_1 = 1{,}4140}$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left(\frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2+\Lambda_{21}x_1}\right)$$
$$= -\ln(0{,}51 + 0{,}5313 \cdot 0{,}49) - 0{,}49 \cdot \left(\frac{0{,}1891}{0{,}49+0{,}1891\cdot 0{,}51} - \frac{0{,}5313}{0{,}51+0{,}5313\cdot 0{,}49}\right)$$
$$= 0{,}4409$$

$\Rightarrow \underline{\gamma_2 = 1{,}5541}$

Similarily to a):

$$P = x_1\gamma_1 P_1^{sat} + x_2\gamma_2 P_2^{sat}$$

$$P = 0{,}49 \cdot 1{,}4140 \cdot 134{,}95 + 0{,}51 \cdot 1{,}5541 \cdot 182{,}79$$

$\boxed{P = 238{,}38 \text{ mmHg}}$

Then, using the modified Raoult's law

$$y_1 = \frac{x_1\gamma_1 P_1^{sat}}{P} = \frac{0{,}49 \cdot 1{,}4140 \cdot 134{,}95}{238{,}38}$$

$\boxed{y_1 = 0{,}392}$

c) Ideal solution $\Rightarrow \gamma_1 = \gamma_2 = 1$

$$P = x_1\gamma_1 P_1^{sat} + x_2\gamma_2 P_2^{sat}$$

$$P = 0{,}49 \cdot 1 \cdot 134{,}95 + 0{,}51 \cdot 1 \cdot 182{,}79$$

$\boxed{P = 159{,}35 \text{ mmHg}}$

$$y_1 = \frac{x_1\gamma_1 P_1^{sat}}{P} = \frac{0{,}49 \cdot 1 \cdot 134{,}95}{159{,}35}$$

$\boxed{y_1 = 0{,}415}$