Exercise 11

1. Raoult's law

Part I – Raoult's Law

a) Give the equation for Raoult's law and define the symbols.

b) What are the major assumptions of Raoult's law?

a) Raoult's law: $y_i P = x_i P_i^{sat}$

- y_i is the mole fraction of component i in the vapor
- x_i is the mole fraction of component i in the liquid
- P is the pressure of the system
- P_i^{sat} is the vapor pressure of pure component i

b) Major assumptions:

- Ideal gas
- Ideal mixture
- low to moderate pressure
- molecules are not too different in size and have the same chemical nature.

Part II – Dewpoint and Bubblepoint Calculations with Raoult's Law

Consider the binary system consisting of methanol (species 1) and methyl acetate (species 2). The vapor pressures for the pure species are given by

$$\ln P_1^{\text{sat}}/[\text{kPa}] = 16.59158 - \frac{3643.31}{T/[\text{K}] - 33.424} \tag{1}$$

$$\ln P_2^{\text{sat}}/[\text{kPa}] = 14.25326 - \frac{2665.54}{T/[\text{K}] - 53.424} \tag{2}$$

In this problem you will generate a Pxy-diagram for the binary system based on Raoult's law.

a) Based on Raoult's law, derive the equation for bubblepoint.

b) Based on Raoult's law, derive the equation for dewpoint.

c) Plot the Pxy-diagram in Python for a temperature of 45 C°. That is, plot P vs. x_1 (bubblepoint) and P vs. y_1 (dewpoint line) in the same graph.

d) Raoult's law can be modified with the activity coefficient γ_i, and thus take into account liquid-phase deviations from ideal solution behavior. This produces a more broadly applicable description of VLE-behavior. The modified Raoult's law is given by:

$$y_i P = x_i \gamma_i P_i^{\text{sat}} \tag{3}$$

For the methanol (1) and methyl acetate (2) mixture, a correction for the activity coefficients is given by

$$\ln \gamma_1 = A x_2^2, \quad \ln \gamma_2 = A x_1^2, \quad A = 2.771 - 0.00523T[\text{K}] \tag{4}$$

Derive the bubblepoint and dewpoint equations based on the modified Raoult's law.

e) Based on the modified Raoult's law, plot the bubblepoint line and dewpoint line in a Pxy-diagram.

f) The modified Raoult's law provies an azeotrope for the chemical system. What does the azeotrope imply?

g) Give the defintion of the relative volatility, α_{12}. What value does α_{12} take at the azeotrope and what impact does this has on a separation process such as distillation?

a) For the system we have:

$$y_1 P = x_1 P_1^{sat}$$

$$y_2 P = x_2 P_2^{sat}$$

Using that $y_1 + y_2 = 1$, and reformulating Raoult's law, we get:

$$y_1 = \frac{x_1 P_1^{sat}}{P}, \quad y_2 = \frac{x_2 P_2^{sat}}{P}$$

$$y_1 + y_2 = 1$$

$$\frac{x_1 P_1^{sat}}{P} + \frac{x_2 P_2^{sat}}{P} = 1 \quad / \cdot P$$

$$\underline{\underline{P = x_1 P_1^{sat} + x_2 P_2^{sat}}} \quad \text{Bubble point}$$

b) Similarily to a):

$$x_1 = \frac{y_1 P}{P_1^{sat}}, \quad x_2 = \frac{y_2 P}{P_2^{sat}}$$

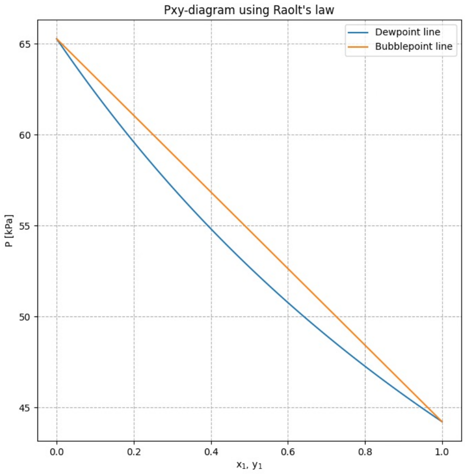
$$x_1 + x_2 = 1$$

$$\frac{y_1 P}{P_1^{sat}} + \frac{y_2 P}{P_2^{sat}} = 1$$

$$P\left(\frac{y_1}{P_1^{sat}} + \frac{y_2}{P_2^{sat}}\right) = 1$$

$$P = \frac{1}{y_1/P_1^{sat} + y_2/P_2^{sat}}$$ Dew point

c)



d) Following the same approach as a) and b)

For the system we have:

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

$$y_2 P = x_2 \gamma_2 P_2^{sat}$$

Using that $y_1 + y_2 = 1$, and reformulating Raoult's law, we get:

$$y_1 = \frac{x_1 \gamma_1 P_1^{sat}}{P}, \quad y_2 = \frac{x_2 \gamma_2 P_2^{sat}}{P}$$

$$y_1 + y_2 = 1$$

$$\frac{x_1 \gamma_1 P_1^{sat}}{P} + \frac{x_2 \gamma_2 P_2^{sat}}{P} = 1 \qquad / \cdot P$$

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

Similarily to dew point:

$$x_1 = \frac{y_1 P}{\gamma_1 P_1^{sat}}, \quad x_2 = \frac{y_2 P}{\gamma_2 P_2^{sat}}$$

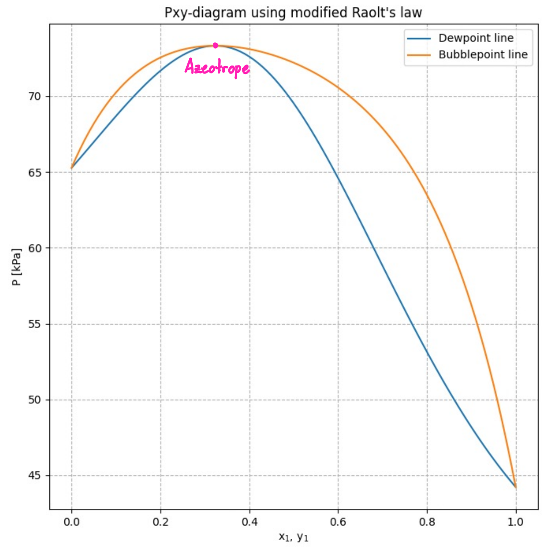
$$x_1 + x_2 = 1$$

$$\frac{y_1 P}{\gamma_1 P_1^{sat}} + \frac{y_2 P}{\gamma_2 P_2^{sat}} = 1$$

$$P\left(\frac{y_1}{\gamma_1 P_1^{sat}} + \frac{y_2}{\gamma_2 P_2^{sat}}\right) = 1$$

$$P = \frac{1}{\frac{y_1}{\gamma_1 P_1^{sat}} + \frac{y_2}{\gamma_2 P_2^{sat}}}$$

e)



f) An azeotrope implies a mixture where the vapor and liquid phases have the same composition. On the graph, this is where the dew- and bubblepoint lines intersect.

g) Relative volatility: $\alpha_{12} = \frac{k_1}{k_2}$

k-value: $k_i = \frac{y_i}{x_i}$

$$\Rightarrow \alpha_{12} = \frac{y_1/x_1}{y_2/x_2}$$

For an azeotrope, $y_1 = x_1$ and $y_2 = x_2$ $\Rightarrow \alpha_{12} = \frac{1}{1} = 1$

This means that both components are equally volatile (likely to be in the gas phase), meaning that it is impossible to separate the components from each other using distillation.

Part III – Calculations with Raoult's Law

1. Use Raoult's law and calculate P and y_i for $T = 45C^{\circ}$ and $x_1 = 0.25$. Compare the result with the modified Raoult's law and provide the error in %.
2. Use Raoult's law and calculate P and x_i for $T = 45C^{\circ}$ and $y_1 = 0.60$. Compare the results with the modified Raoult's law. *Hint*: An iterative solution approach is needed for the modified Raoult's law.

1. Calculating P from the bubble point line, and then inserting into raoults law gives:

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

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

Result:

```
Part III.1:
For Raoult's law:
y1 = 0.1844
P = 60.3588 kPa
For modified Raoult's law:
y1 = 0.2822
P = 73.5003 kPa
The errors are:
Error in y1 = 34.672%
Error in P = 17.879% kPa
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2) Iterating so that the total pressure P from the modified Raoult's law for each component are approximately equal.

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Part III.2:
For Raoult's law:
x1 = 0.6887
P = 51.0893 kPa
For modified Raoult's law:
x1 = 0.8169
P = 62.8945 kPa
The errors are:
Error in y1 = 15.699%
Error in P = 18.770% kPa
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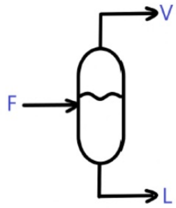
2. Flash calculation using Raoult's law

Let F denote the moles of feed sent into a separator where a flash process takes place. A liquid at a pressure equal to or greater than its bubblepoint pressure flashes or partially evaporates when the pressure is reduced below its bubblepoint pressure. Let L denote the moles of liquid and V the moles of vapor resulting from the flash process.



Flash tank.

Consider a non-reacting system with the following overall mole balance

$$F = V + L = 1 \tag{1}$$

The material balance is

$$z_i = x_i L + y_i V \tag{2}$$

where z_i denotes the overall composition, x_i the liquid-phase composition and y_i the valpor composition of species i. The composition in each phase is constrained by $\sum_i x_i = 1$ and $\sum_i y_i = 1$. The K-factor is given by

$$K_i = y_i / x_i \tag{3}$$

In terms of Raoult's law, $y_i P = x_i P_i^{\text{sat}}$, the K-factor can be written as

$$K_i = P_i^{\text{sat}} / P \tag{4}$$

We will perform a flash calculation based on Raoult's law in this exercise. The calculation will be done using Python with the SciPy library and its function *fsolve*.

Let's consider a binary mixture of pentane (comp.1) and heptane (comp.2). The overall composition is $z_1 = z_2 = 0.5$. The critical properties and acentric factor of the components are:

	pentane	heptane
T_c [K]	469.7	540.3
P_c [MPa]	3.369	2.736
ω [-]	0.249	0.349

The saturation pressure of the pure components can be computed from

$$P_i^{\text{sat}} = P_c \times 10^{[7/3(1+\omega)(1-1/T_r)]} \tag{5}$$

The system is at constant temperature of 60°C. The compressed liquid is brought to a pressure of 0.1 MPa where the flash process takes place. What are the liquid and vapor compositions after the flash separation? Furthermore, what is the vapor-over-feed ratio, VOF=V/F?

We will use a nested function which allows us to share variables with the parent function. The parent function will call *fsolve* to solve the non-linear, or iteration, problem. A guess VOF=0.5 is provided to *fsolve* to initiate the iteration process. See the following incomplete code.

We need to complete the nested function *calcobj* in the above Python code.

In the incomplete Python, determine *obj* which *fsolve* must minimize (i.e. *obj* should approach zero) at convergence.

The correct implementation should result in VOF$=0.28$, $x_1 = 0.37$ and $y_1 = 0.81$.

Increase the flash-pressure from 0.1 MPa to 0.2 MPa. Run the Python code and analyze the results.

Increase the flash-pressure to 0.25 MPa, run the Python code and analyze the results.

Explain why your results are not reasonable.

Rearranging (1) gives: $L = F - V = 1 - V$ (VOF becomes V)

Combining with (2) to eliminate L:

$$Z_i = x_i(1-V) + y_i V$$

$$Z_i = x_i + (y_i - x_i)\cdot V \quad (6)$$

Eliminating x_i with the K-factor: $K_i = \frac{y_i}{x_i} \Rightarrow x_i = \frac{y_i}{K_i}$

Using Raoult's law: $y_i P = x_i P_i^{sat} \Rightarrow \frac{y_i}{x_i} = \frac{P_i^{sat}}{P} = K_i$ (4), we can calculate K_i using (5) as the pressure is known

Inserting the K-factor into (6) eliminates x_i

$$Z_i = \frac{y_i}{K_i} + \left(y_i - \frac{1}{K_i}\right)V$$

$$K_i Z_i = y_i(1 + K_i V - V)$$

$$y_i = \frac{K_i Z_i}{1 + (K_i - 1)V} \quad (7)$$

Finally, using that $\sum y_i = 1 \Rightarrow \sum y_i - 1 = 0$, the final expression becomes:

$$obj = \frac{K_1 Z_1}{1 + (K_1 - 1)V} + \frac{K_2 Z_2}{1 + (K_2 - 1)V} - 1 = 0 \quad (8)$$

Implementing (8) and (5) into the calcobj solves the problem.

```
Flash results at T[K] = 333.15, p = 0.1
Comp. 1 = pentane, Comp. 2 = heptane
VOF = 0.2825149114915437
Composition in liquid: x1 = 0.3771705160004604, x2 = 0.6228294839995375
Composition in vapour: y1 = 0.8119422006207822, y2 = 0.1880577993792229
```

These seem reasonable

```
Flash results at T[K] = 333.15, p = 0.2
Comp. 1 = pentane, Comp. 2 = heptane
VOF = 0.9999999999999957
Composition in liquid: x1 = 0.4645287752158828, x2 = 3.3119045636792346
Composition in vapour: y1 = 0.5000000000000001, y2 = 0.4999999999999878
```

VOF $\approx$ Almost all of the feed is vaporized $\Rightarrow$ We are close to the dew-point line

```
Flash results at T[K] = 333.15, p = 0.25
Comp. 1 = pentane, Comp. 2 = heptane
VOF = 4.168076039642018
Composition in liquid: x1 = 1.1876404459783716, x2 = -0.18764044597837162
Composition in vapour: y1 = 1.0226625426392015, y2 = -0.022662542639201536
```

Here VOF > 1 $\Rightarrow$ We are producing more vapor than the feed into the system, which is impossible

We also have $x_1, y_1 > 1$ and $x_2, y_2 < 0$ which is not possible

Looking at the result from p=0,2, we are outside the two-phase region, which means that phase separation is impossible, and most of the equations used in the calculations are wrong, which is the reason for the error.