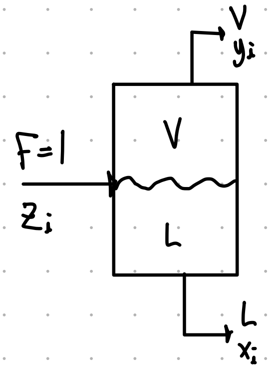
Exercise 12

Problem 1: Modeling and simulation of a flash tank with cubic EOS

In this problem we will model and simulate an isothermal flash tank using the Soave-Redlich-Kwong EOS with the following mixing rules:

$$b_{\text{mix}} = \sum_i x_i b_i$$

$$a_{\text{mix}} = \sum_i \sum_j x_i x_j (1 - k_{ij}) \sqrt{a_i a_j}$$



A binary system of pentane and heptane is to be considered. A partly completed code is attached. The main objective of this problem is to complete this code. The parts that need to be completed are marked with *!...!*.

a) List the required equations that are needed to solve a flash problem with a cubic EOS (here we use Soave-Redlich-Kwong).

b) Use the equations from a) to assist you in completing the attached code. *Hint: The successful code results in, e.g.,* $x_2 \approx 0.6$.

Python code: Flash_EOS_SRK_StudentVersion.py

a) Similarily to raoult's law, the following equations are necessary:

Assuming the feed F=1, then

- Total mole balance:

  $F = V + L = 1$ (1)

- Component mole balances

  $z_i = V y_i + L x_i$ (2)

- Normalization:

  $\sum y_i = 1$ (3)

  $\sum x_i = 1$ (4)

As shown in previous exercises, these equations can be combined into:

We also need $k_i = \frac{y_i}{x_i}$

$$y_i = \frac{z_i k_i}{1 + V(k_i - 1)} \quad (5a)$$

Applying (3)

$$1 = \sum \frac{z_i k_i}{1 + V(k_i - 1)} \quad (5b)$$

From VLE-model for cubic EOS

$$f_{i,V}^{mix} = f_{i,L}^{mix}, \quad \text{where} \begin{cases} f_{i,V}^{mix} = y_i \varphi_{i,V}^{mix} P \\ f_{i,L}^{mix} = x_i \varphi_{i,L}^{mix} P \end{cases}$$

$$\Rightarrow y_i \varphi_{i,V}^{mix} = x_i \varphi_{i,L}^{mix} \quad (6)$$

- The definition of the k-value:

  $k_i = \frac{y_i}{x_i}$, combining with (6) gives:

$$k_i = \frac{\varphi_{i,L}^{mix}}{\varphi_{i,V}^{mix}} \quad (7)$$

- The φ_i can be determined using the equation below:

$$\ln \frac{f_i}{P} = \ln \varphi_i = (Z-1)\frac{B_i}{B_{mix}} - \ln(Z - B_{mix}) - \frac{A_{mix}}{B_{mix}}\left(\frac{2\sqrt{A_i}}{\sqrt{A_{mix}}} - \frac{B_i}{B_{mix}}\right) \ln\left(\frac{Z + B_{mix}}{Z}\right) \quad (8)$$

· In order to start the iteration, we need a guess for k_i, a reasonable guess is raoults law:

$$k_i = \frac{P_i^{sat}}{P} \quad (9)$$

· The nesecary SRK-parameters can be found using:

already implemented

$$\left.\begin{aligned}
a_{mix} &= \sum_i \sum_j x_i x_j (1-k_{ij})\sqrt{a_i a_j} \\
b_{mix} &= \sum_i x_i b_i \\
A_{mix} &= \frac{a_{mix} P}{(RT)^2} \\
B_{mix} &= \frac{b_{mix} P}{RT} \\
A_i &= \frac{a_i P}{(RT)^2} \\
B_i &= \frac{b_i P}{RT}
\end{aligned}\right\} \quad (10)$$

· The polynomial coefficients for the SRK-EOS, $C_0 Z^3 + C_1 Z^2 + C_2 Z + C_3 = 0$:

$$\left.\begin{aligned}
C_0 &= 1 \\
C_1 &= -1 \\
C_2 &= A_{mix} - B_{mix} - B_{mix}^2 \\
C_3 &= -A_{mix} \cdot B_{mix}
\end{aligned}\right\} \quad (11)$$

We also need an equation for guessing new K-values

At equilibrium, $f_{i,V}^{mix} = f_{i,L}^{mix}$

$$y_i \varphi_{i,V}^{mix} \cancel{P} = x_i \varphi_{i,L}^{mix} \cancel{P}$$

$$\Rightarrow \frac{y_i}{x_i} = K_i^{eq} = \frac{\varphi_{i,L}^{mix}}{\varphi_{i,V}^{mix}} \quad (12)$$

Generally, the K-value is given by

$$K_i = \frac{y_i}{x_i} = \frac{f_{i,V}^{mix} / \varphi_{i,V}^{mix} P}{f_{i,L}^{mix} / \varphi_{i,L}^{mix} P} = \frac{f_{i,V}^{mix}}{f_{i,L}^{mix}} \cdot \frac{\varphi_{i,L}^{mix}}{\varphi_{i,V}^{mix}} \overset{(12)}{=} \frac{f_{i,V}^{mix}}{f_{i,L}^{mix}} \cdot K_i^{eq}$$

An expression for K_i^{eq}, or the new guess for K_i will be:

$$K_i^{new} = K_i \cdot \frac{f_{i,L}^{mix}}{f_{i,V}^{mix}} \quad (13)$$

To find f_i^{mix}, the following relations were used:

$$f_i^{mix} = f_i \cdot x_i$$

$$= \varphi_i \cdot x_i \cdot P \quad (14)$$

b) After implementing the equations in a) in the provided code, the output was:

```
x: [0.39978731 0.60021269]
y: [0.82755397 0.17244603]
V: [0.23426953]
L: [0.76573047]
VOF: [0.23426953]
ZV: 0.9660721977783188
ZL: 0.00575254969422928
fV: [0.8037624 0.1634084]
fL: [0.80376221 0.1634084 ]
```

Problem 2: Flash: Raoult's law vs. cubic EOS

a) Explain the differences in the model equations and algorithm for the flash problem when solved using i) the Raoult's law and ii) a cubic EOS.

b) For the same chemical system as in Problem 1, determine the mole fraction compositions of the liquid and vapor phases based on the Raoult's law. What are the relatively differences? Give a comment on these numbers.

a) The difference is that we don't use any of the equations necessary to find the fugacities, only mole/mass balances

The K-value is found using Raoult's law, and we do not check that $f_{i,V}^{mix} = f_{i,L}^{mix}$

For the algorithm, we can say that for Raoult's law, we remove the outer loop.

b) Modifying the program given in Problem 1, by removing all SRK-related parts, the output becomes:

```
x: [0.37958259 0.62041741]
y: [0.81365975 0.18634025]
V: [0.27741015]
L: [0.72258985]
VOF: [0.27741015]
```

- Using Raoult's law, the VOF is higher than for SRK, it also gets higher values for pentane, and lower for heptane
- Comparing which is the most correct is difficult without having the exact solution, but generally, the Raoult's law uses more assumptions than SRK, and will therefore be less accurate.
- Raoult's law assumes low pressures, we have 1 bar, which is relatively low, but this assumption will cause some error.