Solving Nonlinear Systems of Equations (using Symbolic Math Toolbox)

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CME 220

This is an chemical engineering application for solving a set of nonlinear equations for a chloroform(1) + ethanol(2) binary system. The nonlinear system that will be used to solve this problem is shown below.

$$\text{Total Material Balance}: 20 = \dot{L} + \dot{V}$$
$$\text{Chloroform Material Balance}: 4 = x_1\dot{L} + y_1\dot{V}$$
$$\text{Chloroform Modified Raoult's Law}: \ y_1 P = \gamma_1 x_1 P_1^{\text{sat}}$$
$$\text{Ethanol Modified Raoult's Law}: (1 - y_1)P = \gamma_2(1 - x_1)P_2^{\text{sat}}$$

Where:

- P_1^{sat} and P_2^{sat} are the pure component vapor pressures for chloroform and ethanol, respectively.
- $\gamma_1 = \exp\left(A(x_2)^2\right)$
- $\gamma_2 = \exp\left(A(x_1)^2\right)$

Notes about nonlinear system:

- P_1^{sat} and P_2^{sat} will have been previously determined for chloroform and ethanol and will therefore be treated as constants.
- γ_1 and γ_2 represent the activity coefficients for chloroform and ethanol, respectively. The equations that are used to estimate these values comes from the 1-Margules equation.

Relevant Information/Equations used:

The Antoine equation is used to estimate P_i^{sat}:

$$\log_{10}\left(P_i^{\text{sat}}\right) = A - \frac{B}{T + C}$$

Where

- A, B, and C are parameters that fit the pure component vapor pressure data
- T is the boiling point of the pure component (in Celsius)
- P_i^{sat} is the pure component vapor pressure (in mmHg)

Modified Raoult's Law equation is defined as:

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

Where

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

The experimental value of $\frac{\underline{G_E}}{\text{RT}}$ based on experimental data can be found by the below formula:

$$\frac{\underline{G_E}}{\text{RT}} = x_1 \ln(\gamma_1) + x_2 \ln(\gamma_2)$$

Where

- x_1 and x_2 represent the compositions of chloform and ethanol in the liquid phase, respectively.
- $\gamma_1$and γ_2 represent the activity coefficients of chloform and ethanol in the liquid phase, respectively
- $\frac{\underline{G_E}}{\text{RT}}$ is the excess property of the chloroform(1) + ethanol(2) mixture ($\underline{G_E}$) divided by Temperature (T) and the gas constant (R).

The 1-Margules equation is defined as follows:

$$\frac{\underline{G_E}}{\text{RT}} = A x_1 x_2$$

Where

- $\frac{G_E}{\mathrm{RT}}$ is the excess property of the chloroform(1) + ethanol(2) mixture (G_E) divided by Temperature (T) and the gas constant (R).
- A is the 1-Margules equation parameter.
- x_1 and x_2 represent the compositions of chloform and ethanol in the liquid phase, respectively.

The activity coefficients can be determined from the 1-parameter Margules equation as:

$$\ln(\gamma_1) = A(x_2)^2$$

$$\ln(\gamma_2) = A(x_1)^2$$

Where

- x_1 and x_2 represent the compositions of chloform and ethanol in the liquid phase, respectively.
- $\gamma_1$and γ_2 represent the calculated activity coefficients for chloform and ethanol in the liquid phase, respectively

Flash Calculation Problem Description:

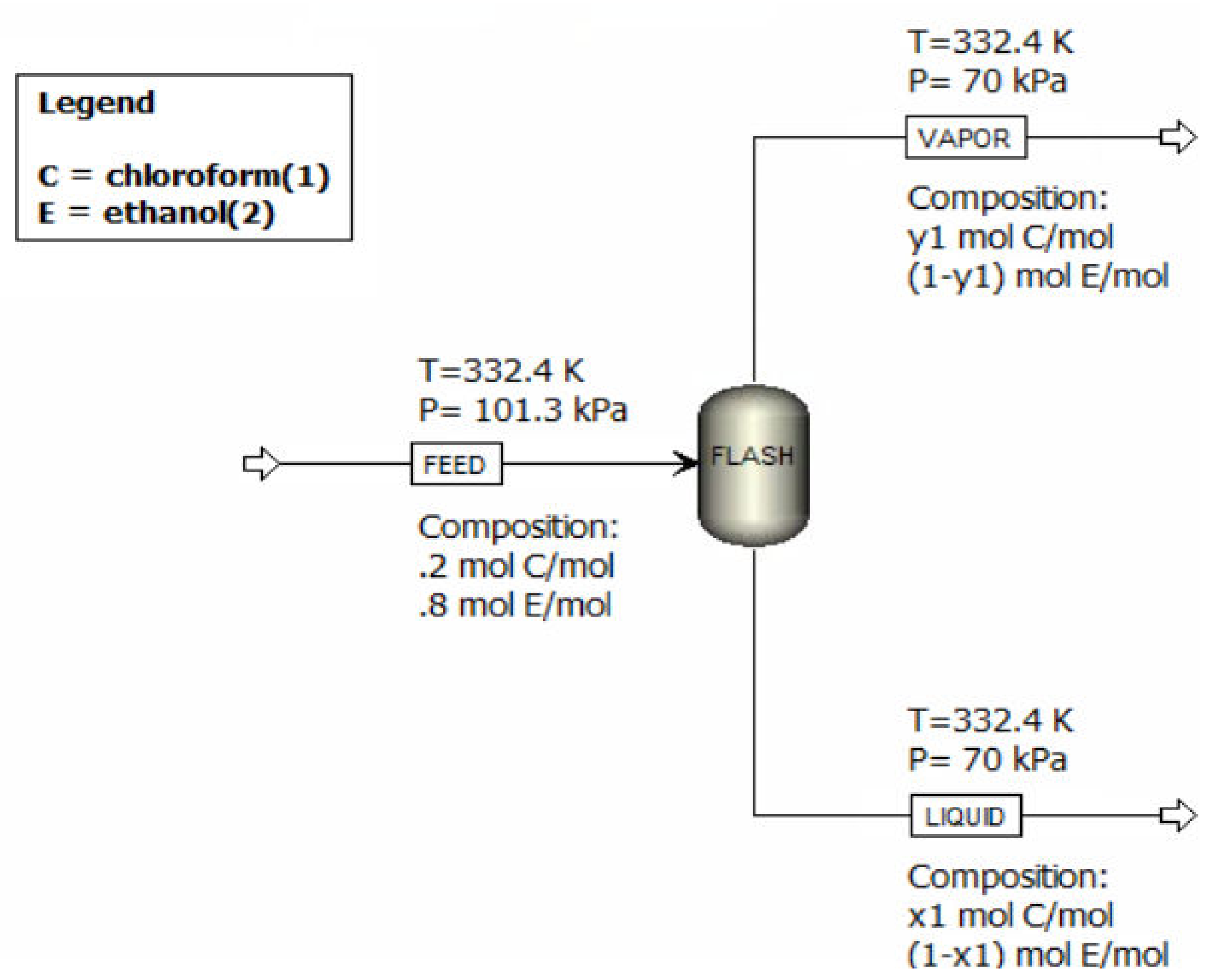
20 mol/min of a mixture of mixture containing 20 mole % chloroform and 80 mole % ethanol at

T = 332.4 K and P = 101.3 kPa and flows into a flash container at T = 332.4 K and P = 70 kPa. The problem requires

that I use the 1-Margules activity coefficient method to find the outlet vapor and liquid feed stream molar flow rates and

compositions.

Flowchart for problem



Define the temperature to be 59.25 C (which is 332.4 K). The temperature needs to be converted to Celsius so that the Antoine equations can be used.

```
Temperature = 332.4-273.15;
```

Define the pressure of the system to be 101.3 kPa

```
Pressure = 101.3;
```

Based on experimental data, the azeotrope of the chloroform(1) + ethanol(2) system was determined to be around x_1 = .84.

```
azeotrope = .84;
```

Estimate the vapor pressure of chloroform and ethanol by using the Antoine parameters from *Fundamentals of Chemical Engineering Thermodynamics* by Dahm and Visco.

In Appendix E, the Antoine parameters for chloroform are A= 6.4934, B= 929.44, and C= 196.03; the Antoine parameters for ethanol are A=8.32109 , B= 1718.10, and C= 237.52.

Convert these pressures from mmHg to kPa.

```
P1sat = 10^(6.4934-929.44/(Temperature+196.03))*(101.325/760);
P2sat = 10^(8.32109-1718.10/(Temperature+237.52))*(101.325/760);
```

Find the γ values by divding the system pressure by vapor pressures of each component. Use those values to then determine the A value for the 1-parameter Margules equation.

Display the$A$ value for the 1-paramter Margules equation.

```
gammaAz = Pressure./[P1sat,P2sat];
A=(azeotrope*log(gammaAz(1))+(1-azeotrope)*log(gammaAz(2)))/((azeotrope)*(1-azeotrope));
fprintf("The A parameter of the 1-parameter Margules equation is around %.2f",A);
```

```
The A parameter of the 1-parameter Margules equation is around 1.36
```

Create four variables as symbolic. L represents the outlet liquid molar flow, V represents the outlet vapor molar flow, x_1 represents the mole fraction of chloroform in the outlet liquid molar flow, and y_1 represents the mole fraction of chloroform in the outlet vapor molar flow. The nonlinear system of equations that will be solved can be found below

$$\text{Total Material Balance}: 20 = \dot{L} + \dot{V}$$

$$\text{Chloroform Material Balance}: 4 = x_1\dot{L} + y_1\dot{V}$$

$$\text{Chloroform Modified Raoult's Law}:\ y_1P = \gamma_1 x_1 P_1^{\text{sat}}$$

$$\text{Ethanol Modified Raoult's Law}: (1-y_1)P = \gamma_2(1-x_1)P_2^{\text{sat}}$$

```
syms L V x1 y1
```

The feed mole percent of chloroform is 20%, and the pressure of the flash system is at P = 70 kPa.

```
molFracFeedChloro = .2;
sysPressure = 70;
```

This section represents the equations used to solve for the four unknown variables (L,V,x_1,y_1).

Equations 1 and 2 represents the total material balance and component material balance for chloroform, respectively.

```
eqn1 = 20 == L + V;
eqn2 = molFracFeedChloro*20 == x1*L + y1*V;
```

Equations 3 and 4 represents the modified Raoult's law equations for chloroform and ethanol, respectively.

For γ_1 and γ_2, I substituted their corresponding 1-parameter Margules expressions into the modified Raoult's Law:

$\gamma_1 = \exp\left(A(x_2)^2\right)$

$\gamma_2 = \exp\left(A(x_1)^2\right)$

```
eqn3 = sysPressure*y1 == x1*P1sat*exp(A*(1-x1)^2);
eqn4 = sysPressure*(1-y1) == (1-x1)*P2sat*exp(A*(x1)^2);
```

I put all the equations into one array and used vpa solve to find the solution for the four unknowns.

```
equations = [eqn1,eqn2,eqn3,eqn4];
sol = vpasolve(equations);
```

Displays the outlet stream molar flows with their respective composition in a table. Create headers that display the phase of the outlet stream and

```
outletstreams = ["Vapor";"Liquid"];
moleflowrates = [round(double(sol.V),1,'decimals');round(double(sol.L),1,'decimals')];
chloroPer = [round(double(sol.y1)*100,1,'decimals');round(double(sol.x1)*100,1,'decimals')];
ethanolPer = [round(double(1-sol.y1)*100,1,'decimals');round(double(1-sol.x1)*100,1,'decimals')


disp(table(outletstreams,moleflowrates,chloroPer,ethanolPer,'VariableNames',...
    {'Outlet stream','Mole flow rate (mol/min)','Chloroform mol %','Ethanol mol %'}))
```

Outlet stream	Mole flow rate (mol/min)	Chloroform mol %	Ethanol mol %
"Vapor"	6.5	40.9	59.1
"Liquid"	13.5	10	90