Department of Chemical and Process Engineering
Thermodynamics

Tutorial Sheet 10: Ideal mixing

1. A liquid mixture of benzene (component 1) and ethylbenzene (component 2) is in equilibrium with its vapour. The vapour pressures of the pure species are given by the following Antoine equations:

$$\ln P_1^{sat}(\text{kPa}) = 13.8858 - \frac{2788.51}{T(°C) + 220.79}$$

$$\ln P_2^{sat}(\text{kPa}) = 14.0045 - \frac{3279.47}{T(°C) + 213.20}$$

Assuming that the vapour phase is an ideal gas and that the liquid phase forms an ideal mixture (i.e., Raoult's Law applies), calculate:

a) The pressure (P) and vapour composition (y_i) at equilibrium when the temperature is 80°C and the mole fraction of ethylbenzene in the liquid phase is 0.6.

b) The pressure (P) and liquid composition (x_i) at equilibrium when the temperature is 100°C and the mole fraction of ethylbenzene in the vapour phase is 0.3.

c) The temperature (T) and liquid composition (x_i) at equilibrium when the pressure is 1 bar and the mole fraction of benzene in the vapour phase is 0.8.

HINT: This requires iteration. To obtain a good initial estimate of the temperature, substitute the equilibrium mixture pressure (given) in the Antoine equations and calculate the saturation temperature for each of the two components at that pressure. The mixture equilibrium temperature must be somewhere between those two values, so a good initial guess is the average of the two values.

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Group 17

1.

a)

$$
\begin{aligned}
P_1^{sat} &= 13.8858 - \frac{2788.51}{80.0 + 220.79} \\
P_1^{sat} &= 101.01 \text{ kPa} \\
P_2^{sat} &= 14.0045 - \frac{3279.47}{80.0 + 213.20} \\
P_2^{sat} &= 16.77 \text{ kPa} \\
P &= x_1 P_1^{sat} + x_2 P_2^{sat} \\
&= 0.4(101.01) + 0.6(16.77) \\
&\boxed{P = 50.466 \text{ kPa}} \\
y_1 &= \frac{x_1 P_1^{sat}}{P} \\
&= \frac{0.6 \cdot 101.01}{50.466} \\
&\boxed{y_1 = 0.8} \\
&\boxed{y_2 = 0.2}
\end{aligned}
$$

b)

$$
\begin{aligned}
P_1^{sat} &= 13.8858 - \frac{2788.51}{100 + 220.79} \\
P_1^{sat} &= 180.04 \text{ kPa} \\
P_2^{sat} &= 14.0045 - \frac{3279.47}{100 + 213.20} \\
P_2^{sat} &= 34.25 \text{ kPa} \\
P &= \frac{1}{\frac{0.3}{34.25} + \frac{0.7}{180.04}} \\
&\boxed{P = 79.07 \text{ kPa}} \\
x_1 &= \frac{y_1 P}{P_1^{sat}} \\
&= \frac{0.3 \cdot 79.07}{34.25} \\
&\boxed{x_1 = 0.69} \\
&\boxed{x_2 = 0.31}
\end{aligned}
$$

c) This question requires iteration to arrive at an appropriate answer but we must first come up with a suitable range for our initial guess of the temperature. To do this we use the hint and calculate the saturation temperature of the antoine equation by rearranging and substituting $P_{equilibrium}$ into P_x^{sat}. Giving;

$$\begin{aligned}
T_{lower} &= \frac{2788.51}{13.8858 - \ln 100} - 220.79 \\
&= 79.68°\text{C} \\
T_{upper} &= \frac{3279.47}{14.0045 - \ln 100} - 213.20 \\
&= 135.7°\text{C} \\
T_0 &= 0.5(T_{lower} + T_{upper}) \\
T_0 &= 107.69°\text{C}
\end{aligned}$$

Then we must create a loop through which we can iterate to get closer to the actual values required, to do this we must set up all of the relevant equations.

$$P_1^{sat}(T) \tag{1}$$

$$P_2^{sat}(T) \tag{2}$$

$$y_1 P_1 = x_1 P_1^{sat} \tag{3}$$

$$y_2 P_2 = x_2 P_2^{sat} \tag{4}$$

$$x_1 + x_2 = 1 \tag{5}$$

Equations 1 and 2 are the Antoine equations given in the question. Equations 3 and 4 are the corresponding Raoult's Law expressions. Equation 5 is the sum of mole fraction equations. The steps for the loop are as follows:

- Get P_1^{sat} from (1)
- Get x_1 from (3)
- Get s_2 from (5)
- Get P_2^{sat} from (4)
- Get T from (2)

Once we obtain T, we can then put it back into step one to run through the loop again, each iteration will get closer and closer to the true values that satisfy the expressions. Plug in the average value as the initial temperature guess. This process can be done by hand but it is better to do it using code, on the next page is the output of a script which automates this process 25 times, along with a graph showing the temperature output of the loop. We can see that initially the temperature is too high, then it is too low, then slightly too high, slightly too low etc. The value eventually converges at a temperature of $\approx 101°$C.

The temperature for iteration 0 = 97.39946313713182
The temperature for iteration 1 = 103.337009478744
The temperature for iteration 2 = 99.50673484919946
The temperature for iteration 3 = 101.82128121520964
The temperature for iteration 4 = 100.36292225874826
The temperature for iteration 5 = 101.2587555144325
The temperature for iteration 6 = 100.69961511950504
The temperature for iteration 7 = 101.04519480376428
The temperature for iteration 8 = 100.8302954803882
The temperature for iteration 9 = 100.96342576600694
The temperature for iteration 10 = 100.88075705924581
The temperature for iteration 11 = 100.93201625800896
The temperature for iteration 12 = 100.90020390036938
The temperature for iteration 13 = 100.91993612074822
The temperature for iteration 14 = 100.90769256841764
The temperature for iteration 15 = 100.9152878700138
The temperature for iteration 16 = 100.91057548388352
The temperature for iteration 17 = 100.91349896686484
The temperature for iteration 18 = 100.91168519485336
The temperature for iteration 19 = 100.91281044974545
The temperature for iteration 20 = 100.9121123334831
The temperature for iteration 21 = 100.9125454445142
The temperature for iteration 22 = 100.91227674056
The temperature for iteration 23 = 100.9124434448625
The temperature for iteration 24 = 100.91234002097957