

1. For the system of ethyl ethanoate(1)/*n*-heptane(2) at 343.15 K,

$$\begin{aligned}\ln \gamma_1 &= 1.150x_2^2 & \ln \gamma_2 &= 1.150x_1^2, \\ P_1^{\text{vap}} &= 79.80 \text{ kPa} & P_2^{\text{vap}} &= 40.50 \text{ kPa}.\end{aligned}$$

Assume you can use low-pressure VLE (i.e., “Modified Raoult’s Law”):

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

and answer the following.

- (a) Compute the bubble-point pressure at $T = 343.15 \text{ K}$, $x_1 = 0.08$.
- (b) Compute the dew-point pressure at $T = 343.15 \text{ K}$, $y_1 = 0.12$.
- (c) What is the azeotrope composition and pressure at $T = 343.15 \text{ K}$?

SOLUTION

- (a) Using Modified Raoult’s Law,

$$\begin{aligned}P &= x_1 \gamma_1 P_1^{\text{vap}} + x_2 \gamma_2 P_2^{\text{vap}} \\ &= x_1 \exp [(1.150)(1 - x_1)^2] P_1^{\text{vap}} + (1 - x_1) \exp [(1.150)x_1^2] P_2^{\text{vap}} \\ &= (0.08)(3.0003)(79.80) + (1 - 0.08)(1.0006)(79.80) = \boxed{54.43 \text{ kPa}}.\end{aligned}$$

- (b) We can cast the Modified Raoult’s law expressions

$$\begin{aligned}y_1 P &= x_1 \gamma_1 P_1^{\text{vap}} \text{ and} \\ P &= x_1 \gamma_1 P_1^{\text{vap}} + x_2 \gamma_2 P_2^{\text{vap}}\end{aligned}$$

into a single equation implicit in x_1 , which for brevity we will refer to as just x (and y instead of y_1):

$$\begin{aligned}y &= \frac{x \gamma_1 P_1^{\text{vap}}}{x \gamma_1 P_1^{\text{vap}} + (1 - x) \gamma_2 P_2^{\text{vap}}} \\ \Rightarrow y(1 - x) \gamma_2 P_2^{\text{vap}} &= (1 - y)x \gamma_1 P_1^{\text{vap}}\end{aligned}$$

We could opt to solve this using a numerical tool like Solver in Excel or `fsoolve` in Python, or your favorite implicit solution method on your graphing calculator. Here, I present a solution using the Newton-Raphson (NR) approach. For NR, we need to construct the function $f(x)$ that evaluates to zero when x satisfies our implicit equation:

$$\begin{aligned}f(x) &= y(1 - x) \gamma_2(x) P_2^{\text{vap}} - (1 - y)x \gamma_1(x) P_1^{\text{vap}}, \text{ where} \\ \gamma_1(x) &= \exp [A(1 - x)^2] \text{ and} \\ \gamma_2(x) &= \exp (Ax^2).\end{aligned}$$

Additionally, we need its derivative df/dx :

$$\begin{aligned}\frac{df}{dx} &= y \left[-\gamma_2 + (1 - x) \frac{d\gamma_2}{dx} \right] P_2^{\text{vap}} - (1 - y) \left[\gamma_1 + x \frac{d\gamma_1}{dx} \right] P_1^{\text{vap}}, \\ &= -y \gamma_2 P_2^{\text{vap}} \left[1 - (1 - x) \frac{d \ln \gamma_2}{dx} \right] - (1 - y) \gamma_1 P_1^{\text{vap}} \left[1 + x \frac{d \ln \gamma_1}{dx} \right], \\ &= -y \gamma_2 P_2^{\text{vap}} [1 - 2Ax(1 - x)] - (1 - y) \gamma_1 P_1^{\text{vap}} [1 - 2Ax(1 - x)] \\ &= -[1 - 2Ax(1 - x)] [y \gamma_2 P_2^{\text{vap}} + (1 - y) \gamma_1 P_1^{\text{vap}}]\end{aligned}$$

NR says that the quantity $x - f/(df/dx)$ is a better approximation to the solution of the implicit equation than is just x . So we follow an iterative strategy in which the "current" value of x is updated to "new" value of x , which then becomes the "current" value to give as another "new" value, and so on. When the absolute value of the correction term $f/(df/dx)$ falls below some tolerance ϵ , then we stop and claim victory.

To begin, we need an initial guess for x . We know that ethanoate (species 1) is much more volatile than *n*-heptane (species 2) at the temperature because it has the higher vapor pressure. So that means that we expect that, in the absence of any azeotropes, that the liquid in equilibrium with a vapor will have a much lower mole fraction of ethanoate than that vapor does. So we expect x to be much less than 0.12. Let's begin with $x = 0.02$ and use a tolerance ϵ of 10^{-6} :

x	γ_1	γ_2	$[1 - 2Ax(1 - x)]$	f	df/dx
0.02000	3.01759	1.00046	0.95492	0.52684	-206.99781
0.02255	3.00036	1.00058	0.94932	0.00301	-204.63418
0.02256	3.00026	1.00059	0.94928	0.00000	-204.62059

So the value of x that satisfies the implicit equation is 0.0226. This is the composition of the droplet of dew that condenses from a vapor with composition $y_1 = 0.12$ at 343.15 K. The pressure at which this condensation occurs is the dew-point pressure:

$$\begin{aligned} P &= x_1 \gamma_1 P_1^{\text{vap}} + x_2 \gamma_2 P_2^{\text{vap}} \\ &= (0.0226)(3.00)(79.80) + (1 - 0.0226)(1.00)(40.50) \\ &= \boxed{45.01 \text{ kPa}}. \end{aligned}$$

(Checking using `fsoe`, I get $x_1 = 0.02256$ at the dew-point.)

- (c) At the azeotrope, we know $x_i = y_i$, so

$$\begin{aligned} y_i P &= x_i \gamma_i P_i^{\text{vap}} \\ \Rightarrow P &= \gamma_i P_i^{\text{vap}} = \gamma_1 P_1^{\text{vap}} = \gamma_2 P_2^{\text{vap}} \\ \Rightarrow \frac{\gamma_1}{\gamma_2} &= \frac{P_2^{\text{vap}}}{P_1^{\text{vap}}} \end{aligned}$$

Note that this final equation appears implicit for x_1 at the azeotrope. However, because

the activity coefficient model is so simple, we can solve for x_1 explicitly:

$$\begin{aligned}
 \gamma_1 &= \frac{P_2^{\text{vap}}}{P_1^{\text{vap}}} \gamma_2 \\
 e^{A(1-x_1)^2} &= \frac{P_2^{\text{vap}}}{P_1^{\text{vap}}} e^{Ax_1^2} \\
 A(1-x_1)^2 &= \ln \frac{P_2^{\text{vap}}}{P_1^{\text{vap}}} + Ax_1^2 \\
 A(1-2x_1+x_1^2-x_1^2) &= \ln \frac{P_2^{\text{vap}}}{P_1^{\text{vap}}} \\
 1-2x_1 &= \frac{1}{A} \ln \frac{P_2^{\text{vap}}}{P_1^{\text{vap}}} \\
 \Rightarrow x_1 &= \frac{1}{2} - \frac{1}{2A} \ln \frac{P_2^{\text{vap}}}{P_1^{\text{vap}}} \\
 &= \frac{1}{2} - \frac{1}{2(1.15)} \ln \left(\frac{40.5}{79.8} \right) = \boxed{0.7949}.
 \end{aligned}$$

Performing a bubble-point pressure calculation at this composition gives the pressure at the azeotrope:

$$\begin{aligned}
 P &= x_1 \gamma_1 P_1^{\text{vap}} + x_2 \gamma_2 P_2^{\text{vap}} \\
 &= (0.7949)(1.0496)(79.8000) + (1 - 0.7949)(2.0681)(40.5000) = \boxed{83.76 \text{ kPa}}.
 \end{aligned}$$

The figure below shows the full Pxy diagram for this binary at ?? K, with the azeotrope labeled.

