Problem 1 *(10 marks) which of the following solutions should have the lowest boiling point? Justify your answer.*

e. 0.01 m sucrose is the answer since sucrose will be in the molecular form in solution. All other choices will dissociate into ions which will increase the effective concentration.

Problem 2 *(10 marks) which of the following solutions should have the lowest freezing point? Justify your answer.*

e. 0.012 m $Ce(NO_3)_4$ is the answer since it will dissociate with the highest concentration of ions which will lead the highest freezing point depression or lowest freezing point.

Problem 3 *(20 marks) what is the osmotic pressure developed if one gram of a protein or polymer of molecular weight 60,000 is dissolved in 100 mL of water and placed in an osmometer at 25° C.*

$$\begin{aligned}\prod &= \frac{RT}{v_{solvent}}\ln x_{solvent} \approx \frac{RT}{v_{solvent}}(1-x_{solvent}) = \frac{RT}{v_{solvent}}x_{solute} \\ &= \frac{RT}{v_{solvent}}\frac{C_{solute}/m_{solute}}{C_{solvent}/m_{solvent}} = RT\frac{C_{solute}}{m_{solute}} \\ &= (8.314)(298.15)\frac{0.01\frac{g}{mL}\times 10^6\frac{mL}{m^3}\times 10^{-3}\frac{kg}{g}}{60\frac{kg}{mol}} = 413.14\ Pa = 4.22\ cm\ H_2O\end{aligned}$$

This analysis is based on the fact that the solute concentration is very low such that

$$x_{\text{solute}} = \frac{\text{Moles solute}}{\text{Moles solute} + \text{Moles solvent}} \approx \frac{\text{Moles solute}}{\text{Moles solvent}} = \frac{C_{\text{solute}}/m_{\text{solute}}}{C_{\text{solvent}}/m_{\text{solvent}}}$$

and

$$\frac{1}{v_{\text{solvent}}} = \frac{C_{\text{solvent}}}{m_{\text{solvent}}}$$

If you prefer to solve the problem in the traditional manner then the solution will be as follows

$$\begin{aligned}\text{moles solute} &= \frac{1}{60000} = 1.6667\times 10^{-5}\text{ mol} \\ \text{moles solvent} &= 100\text{ mL}\frac{1\text{ g}}{1\text{ mL}}\frac{1\text{ mol}}{18\text{ g}} = 5.56\text{ mol} \\ x_1 &= \frac{1.6667\times 10^{-5}}{1.6667\times 10^{-5}+5.56} = 3\times 10^{-6} \\ \prod &= -\frac{(8.314)(298.15)}{18}\ln(1-3\times 10^{-6}) = 413\text{ Pa.}\end{aligned}$$

Problem 4 *(60 marks) Consider the benzene (1) and ethanol (2) system which exhibits an azeotrope at 760 mm Hg and 68.24° C containing 44.8 mole% ethanol. Calculate the composition of the vapor in equilibrium with an equimolar liquid solution at 760 mm Hg given the Antoine constants:*

$$\begin{aligned}\log P_1^{vap} &= 6.87987 - \frac{1196.76}{T+219.61}\\ \log P_2^{vap} &= 8.1122 - \frac{1592.86}{T+226.18}\end{aligned}$$

Use the van Laar equation to describe the activity coefficients in the liquid phase. Trial and errors solution is required; carry out two iterations basing your initial guess on an educated heuristic.

The vapor pressure at the given temperature of 68.24°C

$$\begin{aligned}\log P_1^{\text{vap}} &= 6.87987 - \frac{1196.76}{68.24+219.61} = 2.722\,3 \rightarrow P_1^{\text{sat}} = 10^{2.\,722\,3} = 527.\,59 \text{ mm Hg}\\ \log P_2^{\text{vap}} &= 8.1122 - \frac{1592.86}{68.24+226.18} = 2.\,702 \rightarrow P_2^{\text{sat}} = 10^{2.\,702} = 503.\,5 \text{ mm Hg}\end{aligned}$$

Since this is an azeotrope, we may evaluate the activity coefficients and find the constants in the van Laar equation. The pressure is low enough to justify the use of modified Raoult's law

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

Since $y_i = x_i$ at an azeotropic point, we have

$$\gamma_i = P/P_i^{\text{vap}}$$

so that at $x_1 = 1 - 0.448 = 0.552$

$$\begin{aligned}\gamma_1(x_1 &= 0.552) = P/P_1^{\text{vap}} = 760/527.\,59 = 1.\,440\,5\\ \gamma_2(x_1 &= 0.552) = P/P_2^{\text{vap}} = 760/503.\,5 = 1.\,509\,4\end{aligned}$$

Use the activity coefficients at the azeotropic composition to obtain the van Laar constant

$$\begin{aligned}\alpha &= \ln\gamma_1\left(1+\frac{x_2}{x_1}\frac{\ln\gamma_2}{\ln\gamma_1}\right)^2 = \ln(1.\,440\,5)\left(1+\frac{0.448}{0.552}\frac{\ln(1.\,509\,4)}{\ln(1.\,440\,5)}\right)^2 = 1.\,339\,2\\ \beta &= \ln\gamma_2\left(1+\frac{x_1}{x_2}\frac{\ln\gamma_1}{\ln\gamma_2}\right)^2 = \ln(1.\,509\,4)\left(1+\frac{0.552}{0.448}\frac{\ln(1.\,440\,5)}{\ln(1.\,509\,4)}\right)^2 = 1.\,802\,4\end{aligned}$$

Consequently, the van Laar equations for the activity coefficients model is given by

$$\begin{aligned}\ln\gamma_1 &= \frac{1.\,339\,2}{\left(1+\frac{1.\,339\,2}{1.\,802\,4}\frac{x_1}{x_2}\right)^2} = \frac{1.\,339\,2}{\left(1+0.743\,01\frac{x_1}{x_2}\right)^2}\\ \ln\gamma_2 &= \frac{1.\,802\,4}{\left(1+\frac{1.\,802\,4}{1.\,339\,2}\frac{x_2}{x_1}\right)^2} = \frac{1.\,802\,4}{\left(1+1.\,345\,9\frac{x_2}{x_1}\right)^2}\end{aligned}$$

To compute the composition of vapor in equilibrium with the liquid we use the bubble T method. This is evident that the total pressure and liquid composition are given as equimolar i.e., $x_1 = 0.5$. Assuming that the activity coefficients are independent of temperature in the temperature range of interest (questionable and debatable?!)

$$\begin{aligned}
x_1 &= 0.5 \\
x_2 &= 1 - x_1 = 0.5 \\
\ln \gamma_1 &= \frac{1.3392}{\left(1 + 0.74301 \dfrac{0.5}{0.5}\right)^2} = 0.4408 \rightarrow \gamma_1 = \exp(0.4408) = 1.5539 \\
\ln \gamma_1 &= \frac{1.8024}{\left(1 + 1.3459 \dfrac{0.5}{0.5}\right)^2} = 0.32752 \rightarrow \gamma_1 = \exp(0.32752) = 1.3875
\end{aligned}$$

Using the modified Raoult's law summed over the components present

$$\begin{aligned}
x_1 \gamma_1 P_1^{\text{vap}} + x_2 \gamma_2 P_2^{\text{vap}} &= P \\
0.5(1.5539) P_1^{\text{vap}} + 0.5(1.3875) P_2^{\text{vap}} &= 760 \text{ mm Hg} \\
0.77695 P_1^{\text{vap}} + 0.69375 P_2^{\text{vap}} &= 760 \text{ mm Hg}
\end{aligned}$$

The only unknown in this equation is the temperature since vapor pressure is function of temperature i.e.,

$$\begin{aligned}
760 &= 0.77695 P_1^{\text{vap}} + 0.69375 P_2^{\text{vap}} \\
P_1^{\text{vap}} &= 10^{\left[6.87987 - \frac{1196.76}{T + 219.61}\right]} \\
P_2^{\text{vap}} &= 10^{\left[8.1122 - \frac{1592.86}{T + 226.18}\right]}
\end{aligned}$$

There are two heuristic that can be used to obtain an initial guess for temperature:

- The temperature is a weighted average of the two components pure saturation temperatures

$$\begin{aligned}
T_{\text{boiling},i} &= \frac{B}{A - \log P_i^{\text{vap}}} - C \\
T_{\text{boiling},1} &= \frac{1196.76}{6.87987 - \log_{10} 760} - 219.61 = 79.651^\circ\text{C} \\
T_{\text{boiling},2} &= \frac{1592.86}{8.1122 - \log_{10} 760} - 226.18 = 78.301^\circ\text{C}
\end{aligned}$$

Then the initial guess for the temperature is given by a mole-fraction weighted average

$$\begin{aligned}
T_0 &= \sum x_i T_{\text{boiling},i} = 0.5(79.651) + 0.5(78.301) = 78.976^\circ\text{C} \\
P_1^{\text{vap}} &= 10^{\left(6.87987 - \frac{1196.76}{78.976+219.61}\right)} = 744.35 \text{ mm Hg} \\
P_2^{\text{vap}} &= 10^{\left(8.1122 - \frac{1592.86}{78.976+226.18}\right)} = 780.51 \text{ mm Hg} \\
0.77695(744.35) + 0.69375(780.51) &= 1119.8 > 760
\end{aligned}$$

The assumed temperature yields an estimated total pressure higher than the system total pressure indicating that this temperature is too high. To obtain a refined temperature, we may use any numerical technique such as Newton-Raphson. I am going to use mole fraction normalization instead

$$\begin{aligned}
y_i &= \frac{x_i \gamma_i P_i^{\text{vap}}}{P} \\
y_1 &= \frac{0.77695(744.35)}{760} = 0.76095 \\
y_2 &= \frac{0.69375(780.51)}{760} = 0.71247 \\
y_1 + y_2 &= 0.76095 + 0.71247 = 1.4734
\end{aligned}$$

Again the sum of the mole fraction is higher than unity indicating the temperature is too high. Refine the new temperature using normalized mole fractions i.e.,

$$\begin{aligned}
y_1 &= \frac{0.76095}{1.4734} = 0.51646 = \frac{0.77695 P_1^{\text{vap}}}{760} \\
P_1^{\text{vap}} &= \frac{0.51646(760)}{0.77695} = 505.19 \text{ mm Hg} \\
T_1 &= \frac{1196.76}{6.87987 - \log_{10} 505.19} - 219.61 = 66.942^\circ\text{C} \\
P_1^{\text{vap}} &= 10^{\left(8.1122 - \frac{1592.86}{66.942+226.18}\right)} = 476.52 \text{ mm Hg}
\end{aligned}$$

The corrected pressure is calculated as

$$0.77695(505.19) + 0.69375(476.52) = 723.09 < 760$$

Clearly, the total pressure is higher than the predicted total pressure indicating that the temperature is too low. Correcting again using normalization or may be you want to use interpolation between the two initial guesses

$$\begin{aligned}
y_1 &= \frac{0.77695(505.19)}{760} = 0.51646 \\
y_2 &= \frac{0.69375(476.52)}{760} = 0.43498 \\
y_1 + y_2 &= 0.51646 + 0.43498 = 0.95144
\end{aligned}$$

Again, the sum of mole fractions is below unity indicating that the guessed temperature is too low

$$
\begin{aligned}
y_1 &= \frac{0.516\,46}{0.951\,44} = 0.542\,82 = \frac{0.776\,95 P_1^{\text{vap}}}{760} \\
P_1^{\text{vap}} &= \frac{0.542\,82(760)}{0.776\,95} = 530.\,98 \text{ mm Hg} \\
T_1 &= \frac{1196.76}{6.87987 - \log_{10} 530.\,98} - 219.61 = 68.433^\circ\text{C} \\
P_1^{\text{vap}} &= 10^{\left(8.1122 - \frac{1592.86}{68.433+226.18}\right)} = 507.\,67 \text{ mm Hg}
\end{aligned}
$$

The corrected pressure is calculated as

$$0.776\,95(530.\,98) + 0.693\,75(507.\,67) = 764.\,74 \approx 760$$

This pressure is slightly higher than the system pressure indication that the temperature is higher than the system temperature. However, the difference is too small to justify more hand calculations which is not the case if you are using a computer. Therefore, the temperature is approximately 68.3°C and the mole fractions in the vapor are given as

$$
\begin{aligned}
y_1 &= \frac{0.776\,95(530.\,98)}{760} = 0.542\,82 \\
y_2 &= \frac{0.693\,75(507.\,67)}{760} = 0.463\,42 \\
y_1 + y_2 &= 0.542\,82 + 0.463\,42 = 1.\,006\,2.
\end{aligned}
$$

- Assuming that the azeotrope is flat near that temperature which enables us to use the azeotropic temperature as an initial guess $T = 68.24^\circ$C. This is equivalent to the last iteration. Nevertheless, don't assume that the azeotrope is always flat. There are no guarantees that this is true all the time.