1 (24 points)

Indicate whether each of the following statements is true or false (2 point each) and provide suitable explanations and justifications for each of your answers (4 points each).

A) $\overline{\theta}_i = \left(\frac{\partial[N\theta]}{\partial N_i}\right)_{T,P,N_i \neq N_j}$ Can also be written as $\overline{\theta}_i = \left(\frac{\partial[\theta]}{\partial x_i}\right)_{T,P,x_i \neq x_j}$.

Answer: False.

Why? This is a common mistake when calculating partial molar properties. Since N also changes with N_i, we cannot take N out of the $\partial\left[N\theta\right]$ term and divide N_i by N.

B) $\sum x_i d\phi_i = 0$ By the Gibbs-Duhem relationship.

Answer: False.

Why? The Gibbs-Duhem relationship applies to partial molar properties. ϕ_i is not a partial molar property, so the statement is false. The following is true: $\sum x_i d\ln\phi_i = 0$ as $\ln\phi_i$ is a partial molar property.

C) At equilibrium, a flavoring ingredient dissolved in salad dressing (a phase of oil on a phase of water) would have the same molar concentration.

Answer: False.

Why? At equilibrium, the fugacity of the species in the oil phase and in the water phase would be the same . The molar concentrations, however, need not be equal.

D) The following demand is correct: "I want to set up VLE of a mixture of species A and species B at 100°C and 250 atm, with liquid composition x_A=0.005".

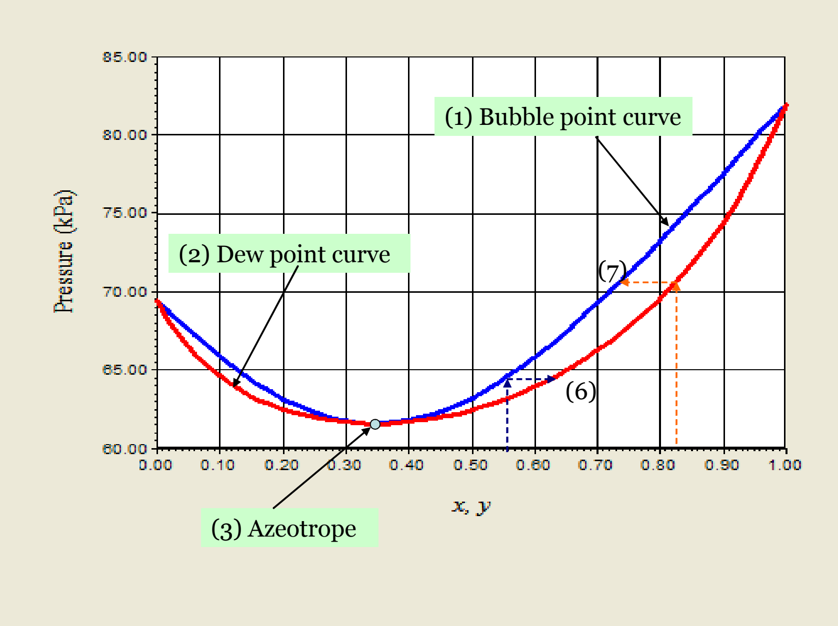
Answer: False.

Why? Phase rule states that only two degrees of freedom (intensive variables) need to be specified to fix the state of a two-phase system with two components. In this case, three variables are specified i.e., the system is over specified.

2 (20 points)

Mark clearly the appropriate number on the figure below for the following:

1. Bubble point curve. Refer to the figure below.
2. Dew point curve. Refer to the figure below.
3. Azeotrope. Refer to the figure below.
4. $x = 0.35, y = 0.35$.
5. Maximum boiling azeotrope: a minimum in the Pxy plane..
6. $x = 0.56, y \approx 0.64$. Refer to the figure below.
7. $y = 0.82, x \approx 0.75$. Refer to the figure below.
8. Component 1 is more volatile since it has a higher vapor pressure.

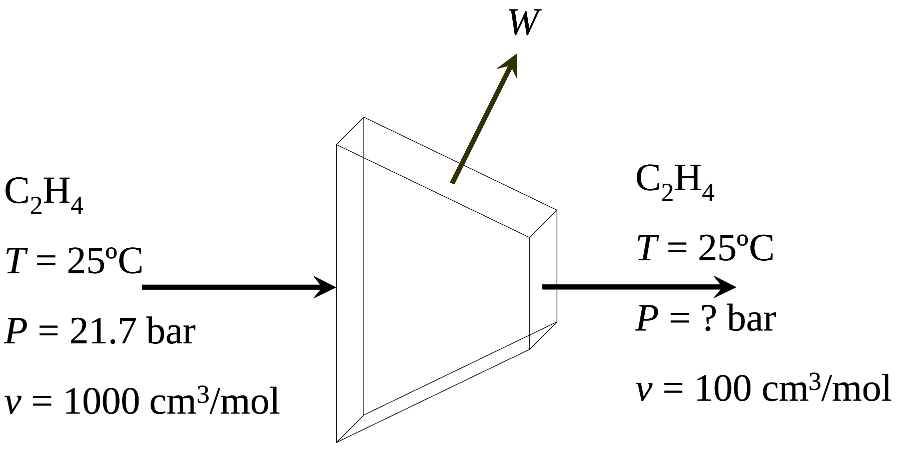


3 (20 points)

Ten moles (10 moles) of ethylene are to be compressed isothermally from their initial state (P = 21.7 bar, T = 25°C, and v = 1000 cm^3/mol) to 100 cm^3/mol. Under these conditions, the behavior of the gas is well described by the Peng-Robinson equation of state.

1. Estimate the pressure at the final state.
2. Estimate the fugacity of ethylene at the final state.

Sketch as below



Obtain the properties of ethylene from any reference you deem useful e.g., Winnick's textbook.

$$\begin{aligned} P &= 21.7 \times 10^5 \text{ Pa} \\ T &= 298.15 \text{ K} \\ v &= 0.0001 \text{ m}^3\text{/mol} \\ T_C &= 282.4 \text{ K} \\ P_C &= 50.4 \times 10^5 \text{ Pa} \\ \omega &= 0.089 \text{ (-)} \\ R &= 8.314 \, \frac{\text{J}}{\text{mol.K}} \end{aligned}$$

$$
\begin{aligned}
b &= 0.07780\frac{RT_C}{P_C} = 0.07780\frac{(8.314)(282.15)}{50.4\times10^5} = 0.0000362 \text{ m}^3/\text{mol}\\
\kappa &= 0.37464 + 1.5422\omega - 0.26992\omega^2 = 0.509\,76\\
\alpha &= \left(\left[1+\kappa\left\{1-\sqrt{\frac{T}{T_C}}\right\}\right]\right)^2 = (1+0.509\,76(1-\sqrt{\frac{298.15}{282.4}}))^2 = 0.972\,15\\
a &= 0.45724\frac{R^2T_C^2}{P_C}\alpha = 0.45724\frac{(8.314)^2(282.15)^2}{50.4\times10^5}(0.97215) = 0.485\,32
\end{aligned}
$$

Calculate the pressure using the PR-EOS an determine the compressibility

$$
\begin{aligned}
P &= \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)}\\
&= \frac{(8.314)(298.15)}{0.0001-0.0000362} - \frac{0.485\,32}{0.0001(0.0001+0.0000362)+0.0000362(0.0001-0.0000362)}\\
&= 8.423\times10^6 \text{ Pa} = 84.23 \text{ bar.}\\
Z &= \frac{Pv}{RT} = \frac{(84.23\times10^5)(0.0001)}{(8.314)(298.15)} = 0.339\,80.
\end{aligned}
$$

Evaluate the fugacity from the PR-EOS

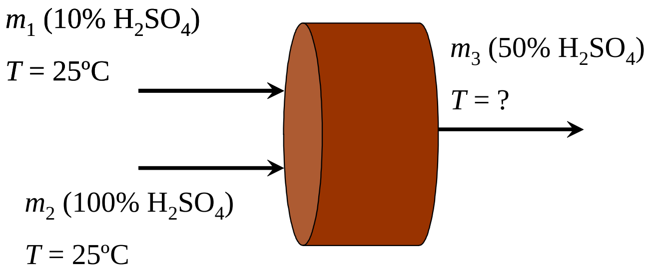
$$
\begin{aligned}
B &= \frac{bP}{RT} = \frac{(0.0000362)(84.23\times10^5)}{(8.314)(298.15)} = 0.12301\\
A &= \frac{aP}{(RT)^2} = \frac{(0.485\,32)(84.23\times10^5)}{(8.314)^2(298.15)^2} = 0.66528\\
\left[\frac{Z^{\mathrm{V}}+(1+\sqrt{2})B}{Z^{\mathrm{V}}+(1-\sqrt{2})B}\right] &= \frac{0.339\,80+(1+\sqrt{2})(0.12301)}{0.339\,80+(1-\sqrt{2})(0.12301)} = 2.2045\\
\ln\frac{f^{\mathrm{V}}}{P} &= \left(Z^{\mathrm{V}}-1\right) - \ln\left(Z^{\mathrm{V}}-B\right) - \frac{A}{2\sqrt{2}B}\ln\left[\frac{Z^{\mathrm{V}}+(1+\sqrt{2})B}{Z^{\mathrm{V}}+(1-\sqrt{2})B}\right]\\
&= (0.339\,80-1) - \ln(0.339\,80-0.12301) - \frac{0.171\,40}{2\sqrt{2}(0.031\,69)}\ln 2.2045\\
&= -0.64301\\
&\rightarrow f^{\mathrm{V}} = 84.23\exp\left[-0.64301\right] = 44.28 \text{ bar.}
\end{aligned}
$$

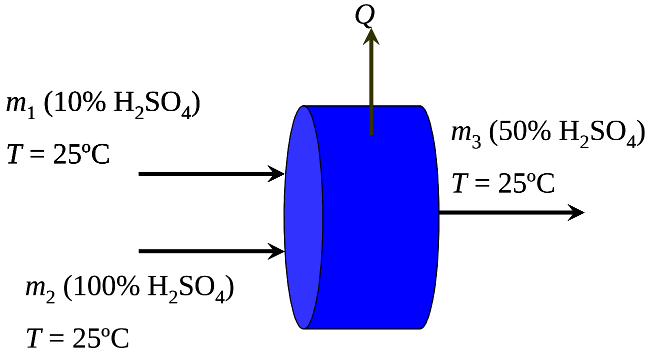
4 (20 points)

A 10 mass % sulfuric acid in water is to be enriched to 50 mass % sulfuric acid solution by adding pure sulfuric acid. Both of the initial solutions are at 25°C.

1. Compute the adiabatic mixing temperature (AMT) for this mixing process.
2. How much heat have to be added / removed to produce the 50 mass % solution at 25°C?

Sketch as below





Overall and sulfuric acid material balances yield for both parts

$$\begin{aligned} m_3 &= m_1 + m_2 \\ 0.5m_3 &= 0.10m_1 + m_2 \end{aligned}$$

From which

$$m_3 = 2\left(0.9m_1\right) = 1.8m_1.$$

Taking 1 kg of the 10% H2SO4 solution ($m_1 = 1$ kg) yields

$$\begin{aligned} m_3 &= (1.8 m_1) = 1.8 \text{ kg} \\ m_2 &= 0.8 \text{ kg.} \end{aligned}$$

Energy balance for the adiabatic case

$$\begin{aligned} \sum_{\text{out}} m_i h_i - \sum_{\text{in}} m_i h_i &= 0 \rightarrow \sum_{\text{out}} m_i h_i = \sum_{\text{in}} m_i h_i \\ m_3 h_3 &= m_1 h_1 + m_2 h_2 \\ h_3 &= \frac{m_1 h_1 + m_2 h_2}{m_3} \end{aligned}$$

Read from the sulfuric acid chart the values of the enthalpy at the inlet condition

$$h_3 = \frac{(1)(25) + (0.8)(20)}{1.8} = 22.8 \text{ kJ/kg.}$$

To find the AMT, all we need to do is to read at the final solution (50% acid) and the value of the enthalpy the final temperature of the solution. The final temperature is about 122°C. The solution is almost at its boiling point temperature!

The isothermal case requires the first law rewritten as

$$\begin{aligned} \sum_{\text{out}} m_i h_i - \sum_{\text{in}} m_i h_i &= Q \\ m_3 h_3 - m_1 h_1 - m_2 h_2 &= Q \\ Q &= (1.8)(-220) - (1)(25) - (0.8)(20) = -437 \text{ kJ.} \end{aligned}$$

This heat has to be removed from the system. The magnitude of heat transfer requirements illustrates the huge heat of mixing for the sulfuric acid - water system.

5 (36 points)

A feed stream of 20% benzene (1) – 80% Toluene (2) is to be flashed at 90°C and 0.65 atm. The vapor pressure of benzene and toluene, at the prescribed temperature, are 1.343 and 0.535 atm respectively.

1. What is the vapor fraction?
2. Determine the composition of the coexisting phases.

Determine the bubble and dew point pressures to check if the system is going to flash or not.

$$\begin{aligned}
P_{\text{bubble}} &= \sum x_i P_i^{\text{vap}} = (0.2)(1.343) + (0.8)(0.535) \\
&= 0.6966 \text{ atm.} \\
P_{\text{dew}} &= \frac{1}{\sum y_i / P_i^{\text{vap}}} = \frac{1}{(0.2)/(1.343) + (0.8)/(0.535)} \\
&= 0.6082 \text{ atm.} \\
P_{\text{dew}} &< P < P_{\text{bubble}}
\end{aligned}$$

Therefore, the system will flash into two vapor and liquid phases.

Calculate the distribution coefficients of both components using

$$\begin{aligned}
K_i &= \frac{P_i^{\text{vap}}}{P} \\
K_1 &= \frac{1.343}{0.65} = 2.0662 \\
K_2 &= \frac{0.535}{0.65} = 0.8231
\end{aligned}$$

Subsequently, formulate the flash equation as

$$\begin{aligned}
F &= F_y - F_x = 0 = \sum \frac{z_i(K_i - 1)}{1 + V(K_i - 1)} \\
0 &= \frac{0.2(2.0662 - 1)}{1 + V(2.0662 - 1)} + \frac{0.8(0.8231 - 1)}{1 + V(0.8231 - 1)} \\
0 &= \frac{0.213\,24}{1.066\,2V + 1} - \frac{0.141\,52}{1 - 0.176\,9V} \\
0 &= \frac{9.430\,5 \times 10^6 V - 3.586 \times 10^6}{9.430\,5 \times 10^6 V^2 - 4.446\,5 \times 10^7 V - 5.0 \times 10^7} \\
0 &= 9.430\,5 \times 10^6 V - 3.586 \times 10^6 \rightarrow V = \frac{3.586 \times 10^6}{9.430\,5 \times 10^6} = 0.380\,26
\end{aligned}$$

The vapor fraction from the feed is $V = 0.380\,26$, and the liquid fraction is $L = 1 - 0.380\,26 = 0.619\,74$. Obtain the mole fractions in the two phases using

$$\begin{aligned}
y_i &= \frac{z_i K_i}{1 + V(K_i - 1)} \\
y_1 &= \frac{(0.2)(2.0662)}{1 + 0.38026(2.0662 - 1)} = 0.29403 \\
y_2 &= 1 - y_1 = 1 - 0.294\,03 = 0.705\,97. \\
x_i &= \frac{z_i}{1 + V(K_i - 1)} \\
x_1 &= \frac{(0.2)}{1 + 0.38026(2.0662 - 1)} = 0.142\,3 \\
x_2 &= 1 - x_1 = 1 - 0.142\,3 = 0.857\,7.
\end{aligned}$$

You can check your answers using a species balance

$$\begin{aligned}
z_i &= x_i L + y_i V \\
z_1 &= 0.142\,3(0.619\,74) + 0.29403(0.38026) = 0.20 \\
z_2 &= 0.857\,7(0.619\,74) + 0.705\,97(0.38026) = 0.80.
\end{aligned}$$