Question 4 (30 points)

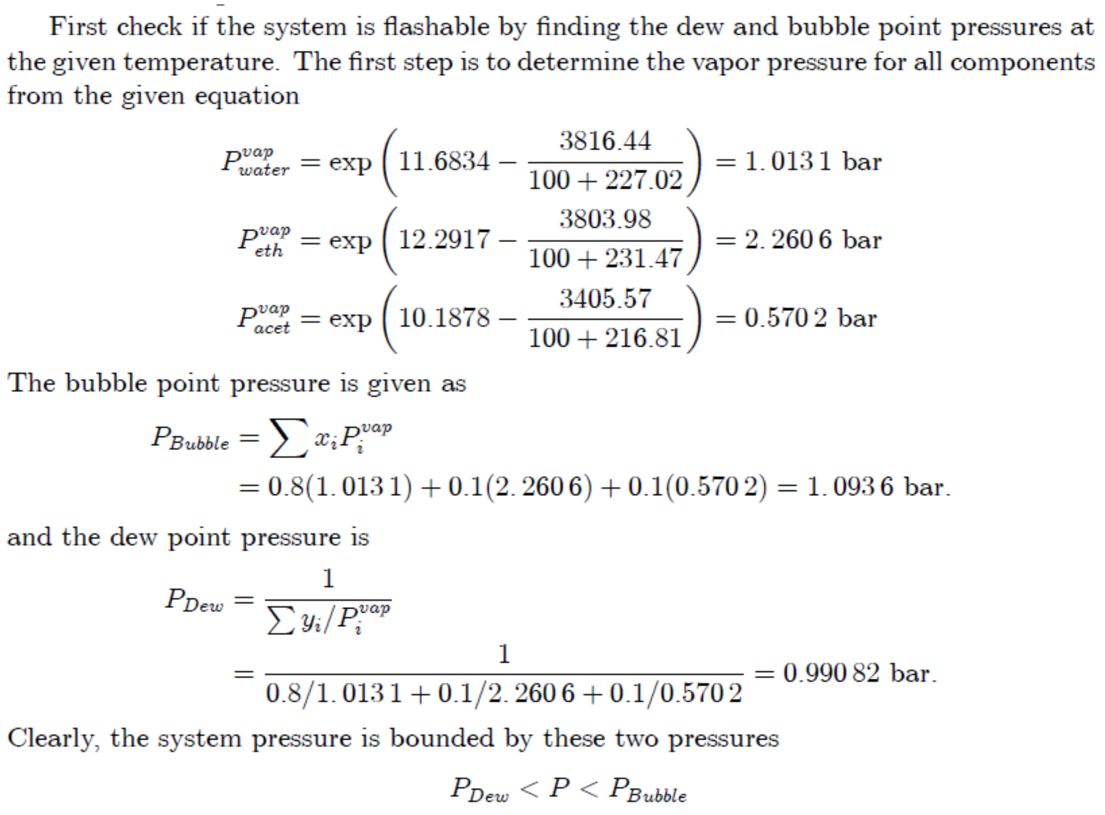
Commonly found products in fermentation are water, ethanol and acetic acid. It is suggested that a mixture of these components fed to a flash separator at 373.15 K and 1 bar will flash and provide some separation. The feed composition and the Antoine equation constants are given in the table below.

	z_i	A	B	C
Water	0.80	11.6834	3816.44	227.02
Ethanol	0.10	12.2917	3803.98	231.47
Acetic acid	0.10	10.1878	3405.57	216.81

The vapor pressure in the Antoine equation is given in the units of bar when temperature is in degrees Celsius

$$\ln P^{\text{vap}}(\text{bar}) = A - \frac{B}{T(^{\circ}\text{C}) + C}$$

a) If the system can be flashed, what are the equilibrium compositions in the vapor phase? Comment on the answers you have calculated.
b) Determine the relative volatilities for each binary system i.e., water/acetic acid, water/ethanol, and acetic acid/ethanol.
c) In your opinion, will it be justified in recommending the use of distillation as a separation technique for such a system?
d) Discuss if Raoult's law can be considered as a good model for such system.



First check if the system is flashable by finding the dew and bubble point pressures at the given temperature. The first step is to determine the vapor pressure for all components from the given equation

$$P_{water}^{vap} = \exp\left(11.6834 - \frac{3816.44}{100 + 227.02}\right) = 1.0131 \text{ bar}$$
$$P_{eth}^{vap} = \exp\left(12.2917 - \frac{3803.98}{100 + 231.47}\right) = 2.2606 \text{ bar}$$
$$P_{acet}^{vap} = \exp\left(10.1878 - \frac{3405.57}{100 + 216.81}\right) = 0.5702 \text{ bar}$$

The bubble point pressure is given as

$$P_{Bubble} = \sum x_i P_i^{vap}$$
$$= 0.8(1.0131) + 0.1(2.2606) + 0.1(0.5702) = 1.0936 \text{ bar}.$$

and the dew point pressure is

$$P_{Dew} = \frac{1}{\sum y_i / P_i^{vap}}$$
$$= \frac{1}{0.8/1.0131 + 0.1/2.2606 + 0.1/0.5702} = 0.99082 \text{ bar}.$$

Clearly, the system pressure is bounded by these two pressures

$$P_{Dew} < P < P_{Bubble}$$

$$0.99082 < 1 < 1.0936$$

and the system will flash and separate. To obtain the equilibrium compositions and the vapor fraction we need to solve the Rachford-Rice equation for this system. To substitute values in the Rachford-Rice equation, we need the distribution coefficients for the components which for the Raoult's law become

$$\begin{aligned} K_i &= \frac{y_i}{x_i} = \frac{P_i^{vap}}{P} \\ K_{water} &= \frac{1.0131}{1} = 1.0131 \\ K_{eth} &= \frac{2.2606}{1} = 2.2606 \\ K_{acet} &= \frac{0.5702}{1} = 0.5702 \end{aligned}$$

The Rachford-Rice equation is given as

$$\begin{aligned} F = F_x - F_y = \sum \frac{z_i(K_i-1)}{1+V(K_i-1)} &= 0 \\ 0 = \frac{0.8(1.0131-1)}{1+V(1.0131-1)} + \frac{0.1(2.2606-1)}{1+V(2.2606-1)} &+ \frac{0.1(0.5702-1)}{1+V(0.5702-1)} \\ 0 = \frac{(7.0977\times10^{-3}V^2 + 9.8566\times10^{-2}V - 0.09356)}{(1.2606V+1)(0.0131V+1)(0.4298V-1)} \end{aligned}$$

The solution to this equation is: $V = 0.89193, V = -14.779$. Since the negative root is unrealistic, the fractional root is the requested root. The vapor fraction, then, is $V = 0.89193$. Now, that we have the vapor fraction, we can proceed to calculate the equilibrium compositions in the vapor and liquid phases

$$\begin{aligned} y_i &= \frac{z_iK_i}{1+V(K_i-1)} \\ y_1 &= \frac{0.8(1.0131)}{1+0.89193(1.0131-1)} = 0.80112 \\ y_2 &= \frac{0.1(2.2606)}{1+0.89193(2.2606-1)} = 0.10641 \\ y_3 &= \frac{0.1(0.5702)}{1+0.89193(0.5702-1)} = 9.2468\times10^{-2} \end{aligned}$$

Similarly for the liquid phase compositions

$$\begin{aligned} x_i &= \frac{z_i}{1+V(K_i-1)} \\ x_1 &= \frac{0.8}{1+0.89193(1.0131-1)} = 0.79076 \\ x_2 &= \frac{0.1}{1+0.89193(2.2606-1)} = 4.7073\times10^{-2} \\ x_3 &= \frac{0.1}{1+0.89193(0.5702-1)} = 0.16217 \end{aligned}$$

Notice, that ethanol is enriched in the vapor phase while acetic acid is being enriched in the liquid phase while water does not show any tendency to be enriched in either phase since its distribution coefficient is essentially unity. The relative volatility can be estimated as

$$
\begin{aligned}
\alpha_{i,j} &= \frac{K_i}{K_j} \\
\alpha_{water,eth} &= \frac{1.0131}{2.2606} = 0.44816 \text{ or } \alpha_{eth,water} = 2.2313 \\
\alpha_{water,acet} &= \frac{1.0131}{0.5702} = 1.7767 \\
\alpha_{eth,acet} &= \frac{2.2606}{0.5702} = 3.9646
\end{aligned}
$$

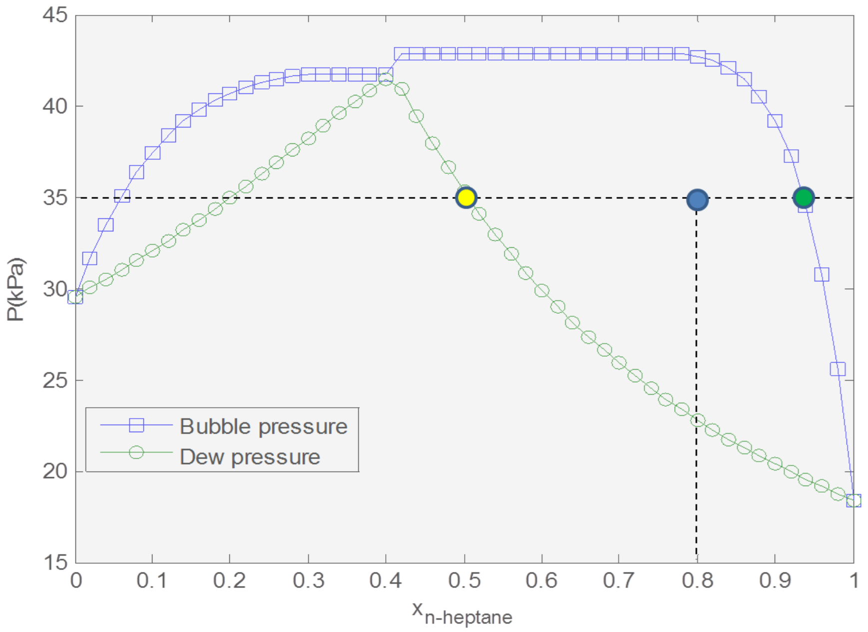
Evidently, these values are higher than unity which makes distillation a separation technique to consider to separate these three components. Raoult's law can't be considered a good model under these conditions since the pressure the components are not similar in shape, size and specific chemical interactions. In fact acetic acid dimerizes in the vapor phase while water hexamerizes in the vapor phase too. The contributions in the liquid phase should be more pronounced.

Component	z	A	B	C	P^{vap}	K	x	y
Water	0.8	11.6834	3816.44	227.02	1.0131	1.0131	0.7908	0.8011
Ethanol	0.1	12.2917	3803.98	231.47	2.2606	2.2606	0.0470	0.1064
Acetic acid	0.1	10.1878	3405.57	216.81	0.5702	0.5702	0.1622	0.0925

2. (10 marks) The binary system n-heptane (1) – ethanol (2) has an azeotrope at P = 42 kPa and x = 0.4. The vapor pressures at T = 50°C are $P_1^{vap} = 16$, and $P_2^{vap} = 29$ kPa. Also, the following points on the bubble and dew curves are known:

x_1	**0.17**	**0.6**	**0.9**
P_{Bubble} (kPa)	**40**	**42**	**39**
y_1	**0.17**	**0.6**	**0.9**
P_{Dew} (kPa)	**34**	**30**	**20**

Sketch on the graph provided below the *Pxy* phase diagram for this binary system.



What is the type of azeotrope this diagram features?

The azeotrope is a minimum boiling azeotrope since the azeotropic pressure is greater than the pure component vapor pressure.

Which component is more volatile: n-heptane or ethanol?

Since ethanol has the larger vapor pressure, it is more volatile.

What is the liquid fraction for a mixture of overall composition x = 0.8 and P = 35 kPa?

Use inverse lever rule to obtain $L = \frac{0.8-0.5}{0.94-0.5} = \frac{0.3}{0.44} = 0.68$

3. (12 marks)

It is suggested that a mixture of components: A, B, and C, fed to a flash separator at 100°C and 1.0 bar will flash and provide some separation. The feed composition and the vapor pressure are given in the table below.

	z_i	P^{vap} (bar)
A	**0.1**	**0.404**
B	**0.5**	**0.417**
C	**0.4**	**2.043**

e) If the system can be flashed, what are the equilibrium compositions in the vapor phase? Fill in the table below and comment on the answers you have calculated.

	K	x	y
A			
B			
C			

f) Determine the relative volatilities for each binary system. Identify which binary system would be the easiest to separate using ordinary distillation. Also, Identify which binary system would be hardest to separate using ordinary distillation.

Binary pair	
$\alpha_{1,2}$	
$\alpha_{1,3}$	
$\alpha_{2,3}$	

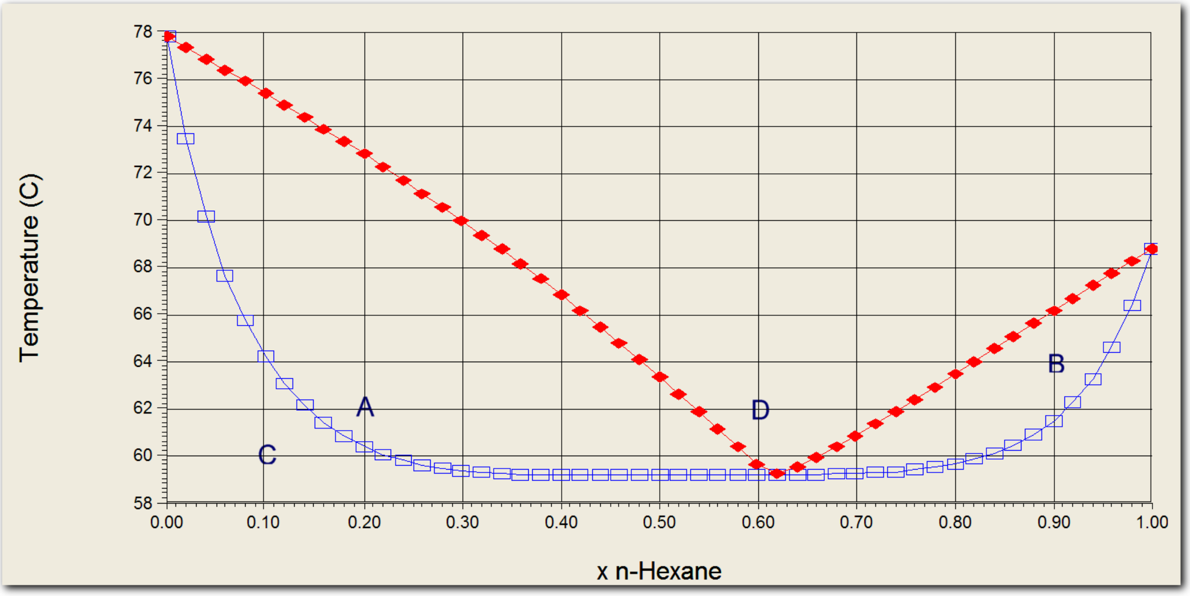
T	**100**
P	**1**
V	**0.108022**

	z_i	*A*	*B*	*C*
A	**0.1**	**11**	**3810**	**220**
B	**0.5**	**11**	**3800**	**220**
C	**0.4**	**11**	**3600**	**250**

Pvap	xPvap	Y/Pvap	K	F				
0.404037	**0.040404**	**0.247502**	**0.404037**	**-0.0637**		a12	0.969233	1.031743
0.416862	**0.208431**	**1.199438**	**0.416862**	**-0.31117**		a13	0.197793	
2.042727	**0.817091**	**0.195817**	**2.042727**	**0.374867**		a23	0.204071	
	1.065925	**0.608733**		**-9E-08**				
	Pbubble	**Pdew**						

x	y
0.106881	0.043184
0.533613	0.222443
0.359506	0.734373
1	1

2. (7 marks) Answer the following questions based on the provided *Txy* phase diagram for the binary system: *n*-hexane (1) and ethanol at a total pressure of one bar.



a) The phase(s) of point C is subcooled liquid.

b) Liquid composition at equilibrium with a vapor composition $y_1 = 0.62$ is 0.62.

c) The relative volatility at $x_1 = 0.62$ is $\alpha_{12} = 1$.

d) The type of azeotrope, if any, is minimum boiling azeotrope.

e) This systems exhibits positive deviations from Raoult's law.

f) The more volatile species is n-hexane and its boiling temperature is = 69°C.

g) The fraction of vapor phase at point A = $\dfrac{0.2-0.14}{0.54-0.14} = \dfrac{0.06}{0.40} = 0.15$.

3. (9 marks)

Commonly found products in fermentation are water (1), ethanol (2) and acetic acid (3). It is suggested that a mixture of these components fed to a flash separator at 90°C and 1.0 bar will flash and provide some separation. The feed composition and the vapor pressure are given in the table below.

	z_i	P^{vap} (bar)
Water	**0.40**	**0.70**
Ethanol	**0.55**	**1.58**
Acetic acid	**0.05**	**0.40**

g) If the system can be flashed, what are the equilibrium compositions in the vapor phase? Fill in the table below and comment on the answers you have calculated.

Vapor fraction = 0.818

	K	x	y
Water	**0.701**	**0.5294**	**0.3712**
Ethanol	**1.582**	**0.3726**	**0.5895**
Acetic acid	**0.402**	**0.0980**	**0.0393**

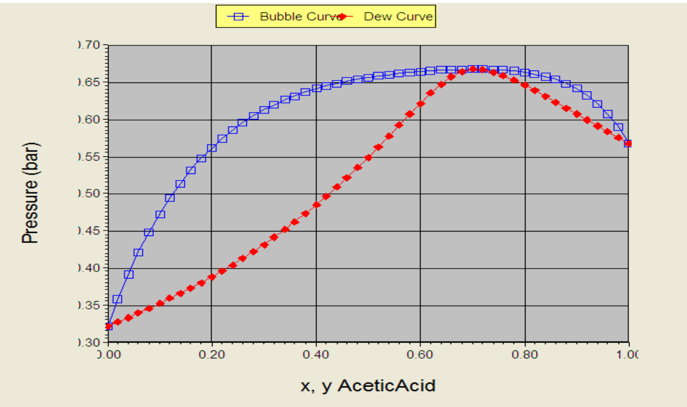
h) Determine the relative volatilities for each binary system i.e., water/ethanol, water/acetic acid, and ethanol/acetic acid. Which binary system would be the easiest to separate using distillation?

Binary pair	
$\alpha_{1,2}$	**0.443 (2.26)**
$\alpha_{1,3}$	**1.75**
$\alpha_{2,3}$	**3.94**

The system with the highest relative volatility is the easiest to be separated by distillation: Ethanol – Acetic acid.

Question 1 (12 points)

a) Sketch a *Pxy* VLE phase diagram for a binary system featuring a minimum boiling azeotrope at $x = 0.7$.



b) The van der Waal’s equation of state is given by:

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

c) Mr. Okla Zaki claims it is justified to assume that Raoult’s law applies for the system: Benzene (1) and n-hexane (2) at 100 bars. Do you think he is right? Justify your answer.

Mr. Okla Zaki is not justified in assuming that Raoult’s law applies for the system: Benzene (1) and n-hexane (2) at 100 bars. The reason is twofold: the pressure is not low enough to justify using the ideal gas mixture for the vapor phase and the two components are not close in shape, size or chemical interactions.

d) Increasing temperature and pressure will increase the solubility of a sparingly soluble gas in a certain solvent. Comment on this statement.

This is not true. It is true that increasing pressure will increase solubility but increasing temperature will decrease solubility.

e) The activity coefficient approaches unity as the concentration of a material approaches unity. Comment on this statement.

This is correct since the material become more ideal as its concentration approaches the pure component limit and its activity as defined by the ratio of fugacity in the mixture to that in the pure component state at the same temperature and pressure approaches the mole fraction.

Question 3 (12 points)

The system: propane (1), *i*-butane (2) and *n*-butane (3), at 27°C, has the overall composition $\mathbf{z} = \{0.4, 0.3, 0.3\}$. Recovery of propane from this mixture is to be carried out by flashing the mixture in a flash drum at the prescribed temperature.

a) Calculate the pressure range for the existence of two phases.
b) If we are to operate the drum at the middle of the calculated pressure range, what is the fraction of the obtained vapor and what is the mole fraction of propane in it? Use Rachford-Rice equation with an initial guess 0.55. Carry out only one iteration and use the result as your final answer for the vapor fraction.
c) Will distillation be a good choice for separating propane (1) from *i*-butane (2) and *n*-butane (3)?
d) Will distillation be a good choice for separating *i*-butane (2) from *n*-butane (3)?

The vapor pressures for the components are given at the prescribed temperature as $\mathbf{P}^{\text{vap}}(\text{kPa}) = \{1002.30, 362.53, 262.30\}$, respectively.

$$P_{\text{Bubble}} = \sum_{i=1}^{3} x_i P_i^{\text{vap}}$$

$$= 0.4(1002.30) + 0.3(362.53) + 0.3(262.30)$$

$$= 588.37 \text{ kPa.}$$

$$P_{\text{Dew}} = \frac{1}{\sum_{i=1}^{3} y_i / P_i^{\text{vap}}}$$

$$= \frac{1}{0.4/(1002.30) + 0.3/(362.53) + 0.3/(262.30)}$$

$$= 421.88 \text{ kPa.}$$

(3 marks)

The mean of the bubble and dew pressures is 505.125 kPa. Thus the flash conditions are set to this pressure and 27°C. Calculate the distribution coefficients using Raoult's law

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

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

$$K_1 = \frac{1002.30}{505.125} = 1.984, K_2 = \frac{362.53}{505.125} = 0.718, K_3 = \frac{262.30}{505.125} = 0.519$$

$$\alpha_{12} = \frac{K_1}{K_2} = \frac{1.984}{0.718} = 2.76, \alpha_{13} = \frac{K_1}{K_3} = \frac{1.984}{0.519} = 3.82, \alpha_{23} = \frac{K_2}{K_3} = \frac{0.718}{0.519} = 1.38$$

(4 marks)

It is clear from the relative volatility values, that it is easy to separate propane (1) from *i*-butane (2) and *n*-butane (3) by ordinary distillation. It is easy to separate *i*-butane (2) and *n*-butane (3) using ordinary distillation since the relative volatility is > 1.05. However, the separation of propane (1) from *i*-butane (2) and *n*-butane (3) is much easier than separating *i*-butane (2) and *n*-butane (3) from each other.

Apply the calculated distribution coefficients with the known feed compositions in the Rachford-Rice equation using the Newton-Raphson technique to improve the initial guess $V = 0.55$:

$$F = F_x - F_y = \sum_{i=1}^{N} \frac{z_i \left(K_i - 1\right)}{1 + V\left(K_i - 1\right)} = 0$$

$$0 = \frac{0.4(1.984 - 1)}{1 + V\left(1.984 - 1\right)} + \frac{0.3(0.718 - 1)}{1 + V\left(0.718 - 1\right)} + \frac{0.3(0.519 - 1)}{1 + V\left(0.519 - 1\right)}$$

		V	**0.55**	
K_i	$z_i(K_i-1)/(1+(K_i-1)V)$	$z_i(K_i-1)^2/(1+(K_i-1)V)^2$	x_i	y_i
1.984258	0.255429	0.16311	0.259514	0.514943
0.717702	-0.10026	0.033504	0.35514	0.254885
0.519277	-0.19605	0.128123	0.407829	0.211776
∑	**-0.0409**	**-0.3247**	**1.02248**	**0.9816**
F	**0.42412**			

The final answer is about $V = 0.425$

		V	**0.42412**	
K_i	$z_i(K_i-1)/(1+(K_i-1)V)$	$z_i(K_i-1)^2/(1+(K_i-1)V)^2$	x_i	y_i
1.984258	0.277756	0.192871	0.282198	0.559954
0.717702	-0.09621	0.030853	0.340804	0.244596
0.519277	-0.18115	0.109385	0.37683	0.195679
∑	**0.0004**	**-0.3331**	**0.99983**	**1.00023**
F	**0.42531**			

Question 2 (8 points)

A gas obeys the equation of state

$$P(v-b)=RT\ .$$

For this gas, b = 0.05 L/mol. Calculate the fugacity coefficient for the gas at 929.64°C and 1000 bar.

First you need to derive the fugacity expression from the given EOS.

$$\varphi=\exp\left[\frac{1}{RT}\int_0^P\left(v-v^{IG}\right)dP\right]=\exp\left[\frac{1}{RT}\int_0^P\left(v-RT/P\right)dP\right]$$

From the given EOS

$$\varphi=\exp\left[\frac{1}{RT}\int_0^P\left(RT/P+b-RT/P\right)dP\right]=\exp\left[\frac{1}{RT}\int_0^P bdP\right]$$

$$=\exp\left[\frac{bP}{RT}\right]$$

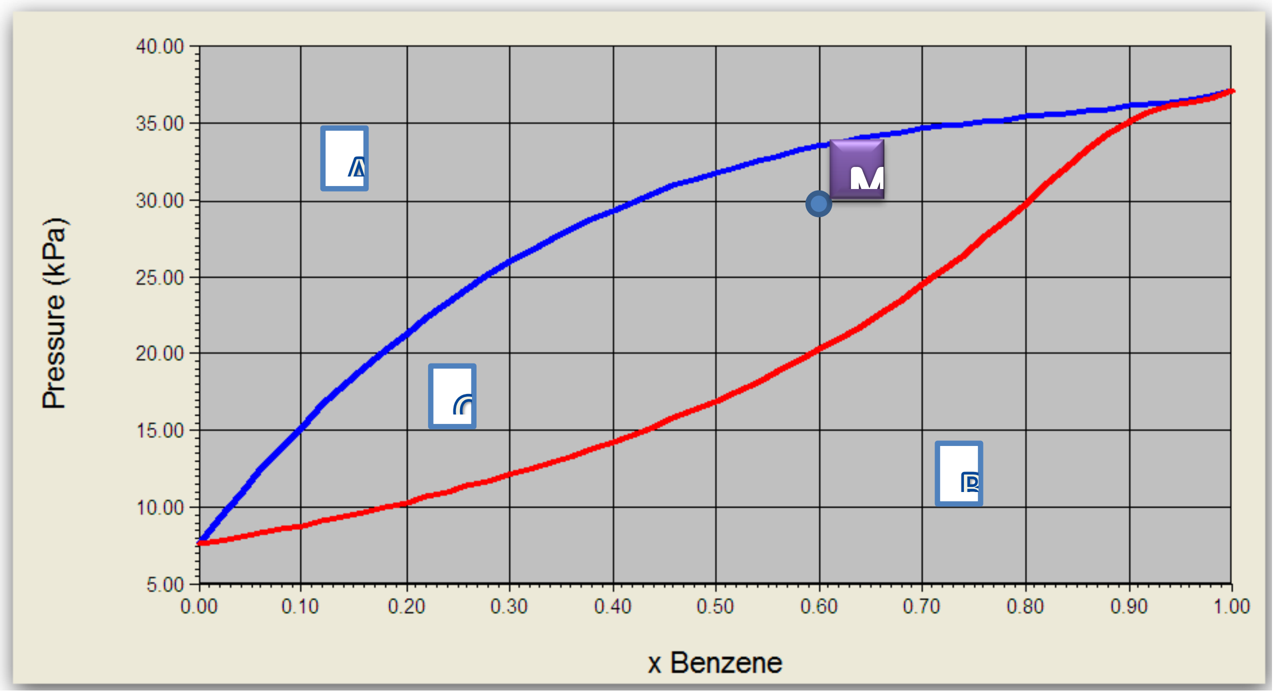
Substitute the given numerical values to obtain

$$\varphi=\exp\left[\frac{(0.05\times10^{-3})(1000\times10^{5})}{8.314(929.64+273.15)}\right]=\exp\left[\frac{5000}{10000}\right]=\exp\left[0.5\right]$$

$$=1.649$$

Question 3 (10 points)

Answer the following questions based on the provided *Pxy* phase diagram for the binary system: Benzene (1) and Comp. (2) at 50°C.



h) The phase(s) of point A is **subcooled liquid**.

i) The phase(s) of point B is **superheated vapor**.

j) Liquid composition at equilibrium with a vapor composition $y_1 = 0.60$ is $x_1 = \mathbf{0.17}$.

k) Vapor composition at equilibrium with a liquid composition $x_1 = 0.10$ is $y_1 = \mathbf{0.43}$.

l) The relative volatility at $x_1 = 0.10$ is $\alpha_{1,2} = \dfrac{y_1/x_1}{y_2/x_2} = \dfrac{(0.43/0.1)}{(0.57/0.9)} = 6.79$.

m) The azeotropic composition, if any, is $x_1 = 0.93$.

n) The type of azeotrope, if any, is **minimum** boiling azeotrope.

o) This system features **positive** deviations from Raoult's law.

p) The vapor pressure of benzene at the prescribed temperature = **37** kPa.

q) The fraction of vapor at point M.

Overall and species material balance assuming a basis of 1 mole

$$\begin{aligned}
1 &= L + V \\
x_{1,M} &= x_1 L + y_1 V \\
x_{1,M} &= x_1(1-V) + y_1 V \\
x_{1,M} - x_1 &= (y_1 - x_1)V \\
V &= \frac{x_{1,M} - x_1}{y_1 - x_1} \\
&= \frac{0.6-0.42}{0.8-0.42} = \frac{0.18}{0.38} = 0.47
\end{aligned}$$

Another way is to use the inverse lever rule with the length from the mixing point

Total length = 3.8 units

Distance from bubble curve to point M = 1.7

Vapor fraction = 1.7/3.8 = 0.45.