Name: **Registration number:**

1. (20 marks)

Select the most correct answer and circle it in the provided answers sheet. More than one answer may be correct, make your choices carefully and wisely.

1.At equilibrium, in a closed isothermal system with a fixed boundary, one of these properties is a minimum

a) S
b) G
c) H
[✓ **d)** A]

2.The mechanical stability criteria dictates that

a) $\kappa_T = 0$
[✓ **b)** $\kappa_T \geq 0$]
c) $\kappa_T < 0$
d) $\kappa_T \leq 0$

3. The Poynting factor is important at

a) Extremely low P
b) High P
c) At low T
[✓ **d)** b and c]

4. The partial molar Gibbs free energy is defined as

a) $\bar{g}_i = \left.\frac{\partial(Ng)}{\partial N_i}\right|_{T,V,N_{j\neq i}}$
b) $\bar{g}_i = \left.\frac{\partial(Ng)}{\partial N_i}\right|_{P,V,N_{j\neq i}}$
[✓ **c)** $\bar{g}_i = \left.\frac{\partial(Ng)}{\partial N_i}\right|_{T,P,N_{j\neq i}}$]
d) $\bar{g}_i = \left.\frac{\partial(NG)}{\partial N_i}\right|_{T,P,N_{j\neq i}}$

5. $\lim_{x_i \to 0}\left(\bar{\theta}_i - \theta_i\right) \to ?$

[✓ **a)** maximum]
b) minimum
c) 0
d) ∞

6.The relative volatility for a certain binary mixture is found to be $\alpha_{1,2}=10$. Therefore, component 1 will most likely concentrate in the vapor phase.

[✓ a) True]
b) False

7. Positive deviations from Raoult's law are manifested on a *Pxy* plot as

a) Bubble curve below Raoult's line
[✓ **b)** Bubble curve above Raoult's line]
c) Dew curve below Raoult's line
d) Dew curve above Raoult's line

8.A system will flash if the system pressure is lower than the dew point pressure and lower than the bubble point pressure

a) True
[✓ b) False]

	(A)	(B)	(C)	(D)
⓿❶	○	○	○	●
⓿❷	○	●	○	○
⓿❸	○	○	○	●
⓿❹	○	○	●	○
⓿❺	●	○	○	○
⓿❻	●	○	○	○
⓿❼	○	●	○	○
⓿❽	○	●	○	○

Problem 2 *(20 marks) Derive the necessary conditions to describe the equilibrium between a supercritical solvent whose fugacity can be calculated using an expression similar to that of vapor fugacity and a pure solid. You may assume that the solid is soluble in the supercritical phase while the supercritical solvent is not soluble in the solid.*

The supercritical phase will be denoted by SC and the solid as s. The solvent will be referred to as component 1 and the solute will be referred to as component 2. The criteria for equilibrium are

1. Thermal equilibrium i.e., equality of temperature in all phases considered
$$T^{\mathrm{SC}} = T^{\mathrm{s}} = T$$
2. Mechanical equilibrium i.e., equality of pressure in all phases considered
$$P^{\mathrm{SC}} = P^{\mathrm{s}} = P$$
3. Chemical equilibrium i.e., equality of fugacity of each component in each phase. The problem statement simplifies the treatment since we need only consider the solute between the supercritical phase and solid
$$\begin{aligned} f_2^{\mathrm{SC}} &= f_2^{\mathrm{s}} \\ y_2 \phi_2 P &= x_2 \phi_2^{\mathrm{sub}} P_2^{\mathrm{sub}} \exp\left[\frac{v_2^{\mathrm{s}}\left(P - P_2^{\mathrm{sub}}\right)}{RT}\right]. \end{aligned}$$

Problem 3 *(20 marks) Use the attached sulfuric acid-water enthalpy chart to solve the following:*

a) What is the boiling point for a 80-wt-% aqueous solution of H_2SO_4 at 0.1 MPa?

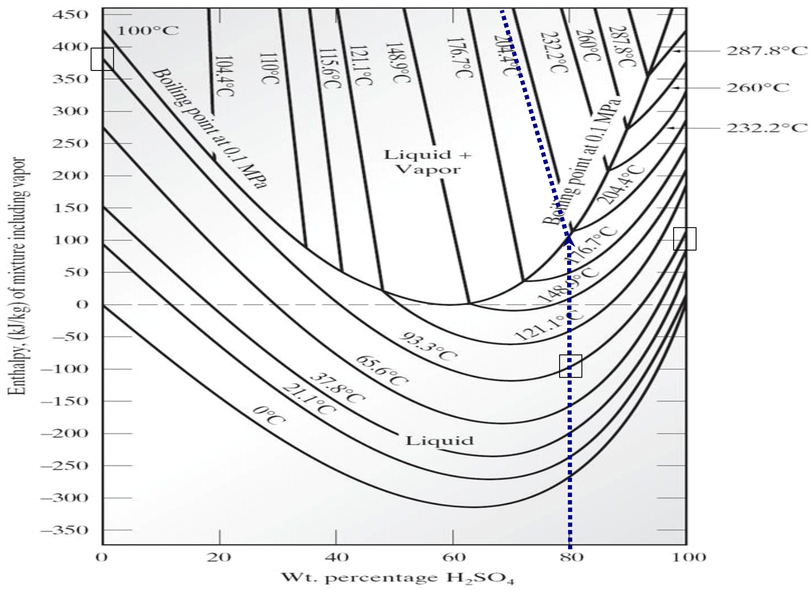
This is read off the chart directly at the boiling point curve (the dotted blue lines). By interpolation yields a value of 200°C at the boiling point of the mixture.

b) What is the heat of mixing for a 80-wt-% aqueous solution of H_2SO_4 at 93.3°C?

The heat of mixing requires knowing the actual enthalpy as well as the pure component enthalpies, taking into consideration that the pressure is kept fixed all the time at 1 bar. Read from the chart the following values: $h_{H_2SO_4}(x = 1.0, T = 93.3°\text{C}) \simeq 110$ kJ/kg, $h_{H_2O}(x = 0, T = 93.3°\text{C}) \simeq 380$ kJ/kg, and $h(x = 0.8, T = 93.3°\text{C}) \simeq -95$ kJ/kg.

$$\begin{aligned}\Delta h_{\text{mix}} &= h(T, P, \mathbf{x}) - \sum x_i h_i(T, P) \\ &= -95 - (0.8)(110) - (0.2)(380) = -259.0 \text{ kJ/kg.}\end{aligned}$$

which indicates that this mixing process is exothermic.



Problem 4 *(40 marks) The reputation of Mr. Okla Zaki as a smart chemineer (chemical engineer) is unsurpassed at the chemical engineering department of the University of Jordan. Mr. Zaki suggested that a mixture of xylene isomers fed to a flash separator at 300 K and 0.012 bars will flash and provide some separation of these isomers. The feed composition and the Antoine equation constants are given in the table below.*

Species	z_i	*A*	*B*	*C*
m-Xylene	*0.4*	*9.5188*	*3366.99*	*-58.04*
o-Xylene	*0.2*	*9.4954*	*3395.57*	*-59.46*
p-Xylene	*0.4*	*9.4761*	*3346.65*	*-57.84*

The Antoine equation is given in the units of bar when temperature is in Kelvin

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

1. If the system can be flashed, what are the equilibrium compositions in the vapor phase? Comment on the answers you have calculated.
   Determine if the given pressure falls between the dew and bubble pressures. This requires determining the vapor pressure for each species at the prescribed temperature

$$P^{\text{vap}}_{\text{m-xylene}} = \exp\left[9.5188 - \frac{3366.99}{300 - 58.04}\right] = 0.012318 \text{ bar}$$
$$P^{\text{vap}}_{\text{o-xylene}} = \exp\left[9.4954 - \frac{3395.57}{300 - 59.46}\right] = 0.009842 \text{ bar}$$
$$P^{\text{vap}}_{\text{p-xylene}} = \exp\left[9.4761 - \frac{3346.65}{300 - 57.84}\right] = 0.012986 \text{ bar}$$

From this vapor pressure and knowledge of the feed composition the bubble and dew pressures are caculated as below

$$\begin{aligned} P_{\text{Bubble}} &= \sum x_i P^{\text{vap}}_{\text{i}} \\ &= 0.4(0.012318) + 0.2(0.009842) + 0.4(0.012986) = 0.012090 \text{ bar} \\ P_{\text{Dew}} &= \frac{1}{\sum y_i/P^{\text{vap}}_{\text{i}}} \\ &= \frac{1}{0.4/(0.012318) + 0.2/(0.009842) + 0.4/(0.012986)} = 0.011962 \text{ bar} \end{aligned}$$

The criterion to check to see whether the system will flash or not is

$$P_{\text{Dew}} < P < P_{\text{Bubble}}$$
$$0.011962 < 0.012 < 0.012090$$

The criterion is true, hence we may proceed to use flash calculation to determine the coexisting compositions in the vapor and liquid phases. We need to use the Rachford-Rice equation first to determine the vapor fraction

$$\mathbf{K} = \frac{\mathbf{P}^{\text{vap}}}{P} = \{1.026512, 0.820208, 1.082154\}$$

$$\begin{aligned}F &= \sum \frac{z_i(K_i - 1)}{1 + V(K_i - 1)} = 0 \\ &= \frac{0.4(1.026512 - 1)}{1 + V(1.026512 - 1)} + \frac{0.2(0.820208 - 1)}{1 + V(0.820208 - 1)} + \frac{0.4(1.082154 - 1)}{1 + V(1.082154 - 1)} = 0\end{aligned}$$

Solution using Matlab's `fzero` with an initial guess of $V = 0.5$ converges at $V = 0.731323$. Consequently,

$$\begin{aligned}y_i &= \frac{z_i K_i}{1 + V(K_i - 1)} \\ y_{\text{m-xylene}} &= \frac{0.4(1.026512)}{1 + 0.731323(1.026512 - 1)} = 0.402\,80 \\ y_{\text{o-xylene}} &= \frac{0.2(0.820208)}{1 + 0.731323(0.820208 - 1)} = 0.188\,88 \\ y_{\text{p-xylene}} &= \frac{0.4(1.082154)}{1 + 0.731323(1.082154 - 1)} = 0.408\,33\end{aligned}$$

and

$$\begin{aligned}x_i &= \frac{z_i}{1 + V(K_i - 1)} \\ x_{\text{m-xylene}} &= \frac{0.4}{1 + 0.731323(1.026512 - 1)} = 0.392\,39 \\ x_{\text{o-xylene}} &= \frac{0.2}{1 + 0.731323(0.820208 - 1)} = 0.230\,28 \\ x_{\text{p-xylene}} &= \frac{0.4}{1 + 0.731323(1.082154 - 1)} = 0.377\,33.\end{aligned}$$

The flash separation will slightly enrich o-xylene and remove p-xylene in the liquid phase while keeping the mole fraction of m-xyelene essentially constant. Nevertheless, the opposite is taking place in the vapor phase: the mole fraction of m-xylene and p-xylene is essentially the same as that in the feed while that of o-xylene is reduced.

2. Determine the relative volatilities for each binary system i.e., m-xylene/o-xylene, m-xylene/p-xylene, o-xylene/p-xylene.

$$
\begin{aligned}
\alpha_{\text{m-xylene,o-xylene}} &= \frac{K_{\text{m-xylene}}}{K_{\text{o-xylene}}} = \frac{1.026512}{0.820208} = 1.2515 \\
\alpha_{\text{m-xylene,p-xylene}} &= \frac{K_{\text{m-xylene}}}{K_{\text{p-xylene}}} = \frac{1.026512}{1.082154} = 0.9486 \\
&\rightarrow \alpha_{\text{p-xylene,m-xylene}} = 1/0.9486 = 1.054\,2 \\
\alpha_{\text{o-xylene,p-xylene}} &= \frac{K_{\text{o-xylene}}}{K_{\text{p-xylene}}} = \frac{0.820208}{1.082154} = 0.7579 \\
&\rightarrow \alpha_{\text{p-xylene,o-xylene}} = 1/0.7579 = 1.319\,4.
\end{aligned}
$$

   These values suggest that p-xylene will be the component concentrated most in the vapor phase followed by m-xylene and least concentrated in the vapor phase will be o-xylene. The opposite order will be in the liquid phase. This order is exactly what was obtained in the flash calculations.

3. In your opinion, will chemineer Zaki be justified in recommending to use distillation as a separation technique for such a system?
   The smart chemineer will be right if he wanted to separate p-xylene from o-xylene. However, the m-xylene will be distributed between the phases. It would be difficult to separate the m-xylene using distillation! Usually, these isomers are separated using crystallization rather than distillation.

4. Discuss if Raoult's law can be considered as a good model for such system.
   Raoult's law would be a good model since these isomers are similar in size, shape and chemical interactions. Also, the pressure in the calculations is so low to justify the use of the IGM model for the vapor phase. A very strong evidence to support such a model is the very close dew and bubble point pressures!

The following table is a summary of the claculations used throughout this problem:

Species	z_i	P^{vap} (bar)	K	x	y
m-Xylene	0.4000	0.0123	1.0265	0.3924	0.4028
o-Xylene	0.2000	0.0098	0.8202	0.2303	0.1889
p-Xylene	0.4000	0.0130	1.0822	0.3773	0.4083