UNIVERSITY OF JORDAN
CHEMICAL ENGINEERING DEPARTMENT

Student name:
Registration number:

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Fill the circles completely.
Don't fill more than one circle for each question. If there are more than one circles filled, you will get a zero for that question.
No answers on the questions sheet will be accepted.
Use a black/blue pen not a pencil.

Question 2. Fugacity by different methods

Steam Tables

Find the enthalpies and entropies for the vapor at the saturation conditions from steam tables

$$\begin{aligned} h(100^{\circ}\text{C}, 1\text{ atm}) &= 2675.43\ \frac{\text{kJ}}{\text{kg}} \\ s(100^{\circ}\text{C}, 1\text{ atm}) &= 7.3598\ \frac{\text{kJ}}{\text{kg.}^{\circ}\text{C}} \\ g(100^{\circ}\text{C}, 1\text{ atm}) &= h(100^{\circ}\text{C}, 1\text{ atm}) - Ts(100^{\circ}\text{C}, 1\text{ atm}) \\ &= 2675.43 - (373.15)(7.3598) = -70.879\ \frac{\text{kJ}}{\text{kg}} \\ &= -70.879\ \frac{\text{J}}{\text{g}} \times 18.015\frac{\text{g}}{\text{mol}} = -1276.9\frac{\text{J}}{\text{mol}}. \end{aligned}$$

Evaluate the ideal gas Gibbs free energy at the given temperature. The lowest pressure is 1 kPa

$$\begin{aligned} h(100^{\circ}\text{C}, 1\text{ kPa}) &= 2688.63\ \frac{\text{kJ}}{\text{kg}} \\ s(100^{\circ}\text{C}, 1\text{ kPa}) &= 9.51356\frac{\text{kJ}}{\text{kg.}^{\circ}\text{C}} \\ g^{IG}(100^{\circ}\text{C}, 1\text{ kPa}) &= h^{IG}(100^{\circ}\text{C}, 1\text{ kPa}) - Ts^{IG}(100^{\circ}\text{C}, 1\text{ kPa}) \\ &= h^{IG}(100^{\circ}\text{C}, 1\text{ kPa}) - Ts^{IG}(100^{\circ}\text{C}, 1\text{ kPa}) \\ &= (2688.63 - (373.15)(9.51356)) \times 18.015 = -15517\frac{\text{J}}{\text{mol}} \\ g^{IG}(100^{\circ}\text{C}, P) &= g^{IG}(100^{\circ}\text{C}, P^{*} = 1\text{ kPa}) + \int_{P^{*}}^{P} v^{IG} dP \\ &= g^{IG}(100^{\circ}\text{C}, P^{*} = 1\text{ kPa}) + RT \ln \frac{P}{P^{*}} \\ &= -15517 + (8.314)(373.15) \ln \frac{101325}{1000} \\ &= -15517 + 14328 = -1189.0\frac{\text{J}}{\text{mol}}. \end{aligned}$$

Determine the fugacity coefficient from its definition as

$$\begin{aligned} \phi &= \exp\left[\frac{g(T,P) - g^{IG}(T,P)}{RT}\right] \\ &= \exp(\frac{-1276.9 + 1189.0}{(8.314)(373.15)}) = \exp(-2.8333 \times 10^{-2}) = 0.97206. \end{aligned}$$

Generalized charts

Find the reduced temperature and pressure as

$$\begin{aligned} T_r &= \frac{T}{T_C} = \frac{373.15}{647.3} = 0.576 \\ P_r &= \frac{P}{P_C} = \frac{0.101325}{22.12} = 4.5807 \times 10^{-3} \end{aligned}$$

Reading the chart is difficult since the value of reduced pressure is too low. Nevertheless, common sense *leads to a unity value of the fugacity coefficient*.

Peng-Robinson EOS

Component	MW (g/mol)	T_c (K)	P_c (MPa)	ω (-)
Water	18.015	647.3	22.12	0.344

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$$
\begin{aligned}
b &= 0.07780\frac{RT_C}{P_C} = 1.89265 \times 10^{-5}, \\
\kappa &= 0.37464 + 1.5422\omega - 0.26992\omega^2 = 0.873216 \\
\alpha(T) &= \left\{1 + \kappa\left[1 - \left(\frac{T}{T_C}\right)^{1/2}\right]\right\}^2 = 1.46463 \\
a(T) &= 0.45724\frac{R^2T_C^2}{P_C}\alpha(T) = 0.876901.
\end{aligned}
$$

$$
\begin{aligned}
B &= \frac{bP}{RT} = 6.18127 \times 10^{-4} \\
A &= \frac{aP}{(RT)^2} = 0.00923100
\end{aligned}
$$

$$
\begin{aligned}
0 &= Z^3 + a_2Z^2 + a_1Z + a_0 \\
a_2 &= B - 1 = -0.999382, \\
a_1 &= A - 3B^2 - 2B = 0.00799360, \\
a_0 &= -AB + B^2 + B^3 = -0.00000532361,
\end{aligned}
$$

Newton-Raphson iteration with an ideal gas compressibility initial guess yields

```
iter xold xnew func deriv check
1 1 0.9915 0.008606 1.009 0.008528
2 0.9915 0.9913 0.0001449 0.9753 0.0001485
3 0.9913 0.9913 4.357e-008 0.9747 4.47e-008
```

Clearly, steam behaves close to an ideal gas at these conditions with a $Z = 0.9913$. The fugacity coefficient for the PR-EOS is defined as

$$
\begin{aligned}
\ln\frac{f}{P} &= (Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2}B}\ln\left[\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B}\right] \\
\ln\frac{f}{P} &= (0.9913 - 1) - \ln(0.9913 - 6.18127 \times 10^{-4}) \\
&\quad - \frac{0.00923100}{\sqrt{8}(6.18127 \times 10^{-4})}\ln\left[\frac{0.9913 + (1+\sqrt{2})(6.18127 \times 10^{-4})}{0.9913 + (1-\sqrt{2})(6.18127 \times 10^{-4})}\right] \\
&= -8.6444 \times 10^{-3} \rightarrow \phi = \frac{f}{P} = \exp(-8.6444 \times 10^{-3}) = 0.9914.
\end{aligned}
$$

Equality of fugacity between vapor and liquid

The vapor fugacity is estimated in the first part. All you need to do is calculate the fugacity in the liquid phase. Find the enthalpy and entropy of liquid from steam tables

$$\begin{aligned}
h(100^\circ\text{C}, 1\text{ atm}) &= 417.51\,\frac{\text{kJ}}{\text{kg}} \\
s(100^\circ\text{C}, 1\text{ atm}) &= 1.3027\,\frac{\text{kJ}}{\text{kg.}^\circ\text{C}} \\
g(100^\circ\text{C}, 1\text{ atm}) &= h(100^\circ\text{C}, 1\text{ atm}) - Ts(100^\circ\text{C}, 1\text{ atm}) \\
&= 417.51 - (373.15)(1.3027) = \frac{\text{kJ}}{\text{kg}} \\
&= -68.593\,\frac{\text{J}}{\text{g}} \times 18.015\frac{\text{g}}{\text{mol}} = -1235.7\frac{\text{J}}{\text{mol}}.
\end{aligned}$$

The ideal gas Gibbs free energy is calculated in the first part as $-1189.0\frac{\text{J}}{\text{mol}}$. Determine the fugacity coefficient from its definition as

$$\begin{aligned}
\phi &= \exp\left[\frac{g(T,P) - g^{IG}(T,P)}{RT}\right] \\
&= \exp\left(\frac{-1235.7 + 1189.0}{(8.314)(373.15)}\right) = \exp(-1.5053 \times 10^{-2}) = 0.98506.
\end{aligned}$$

The vapor and liquid fugacity coefficients are practically equal within the accuracy of the steam tables.

The value of the fugacity coefficient is almost the same between the three methods. This is essentially due to the low pressure which approaches ideality. Nevertheless, this is not to be expected at higher pressures.

Question 3. Sulfuric acid mixtures

a) Take a basis of 1 kg solution which has 0.4 kg H_2SO_4 and 0.6 kg H_2O. The enthalpy at $21.1°$C of pure H_2SO_4 is $h \simeq 10$ kJ/kg, and that of water is $h \simeq 95$ kJ/kg. The first law for an adiabatic process with no work reduces to

$$\begin{aligned} h_{\text{Final}} &= h_{\text{Initial}} \\ h_{\text{Final}} &= 0.4(10) + 0.6(95) = 61.0 \text{ kJ/kg.} \end{aligned}$$

Reading the final temperature off the chart gives a value of $114°$C at almost the boiling point of the mixture.

b) This read off the chart directly at the boiling point curve (the dotted blue lines). By interpolation yields a value of 140°C at the boiling point of the mixture.

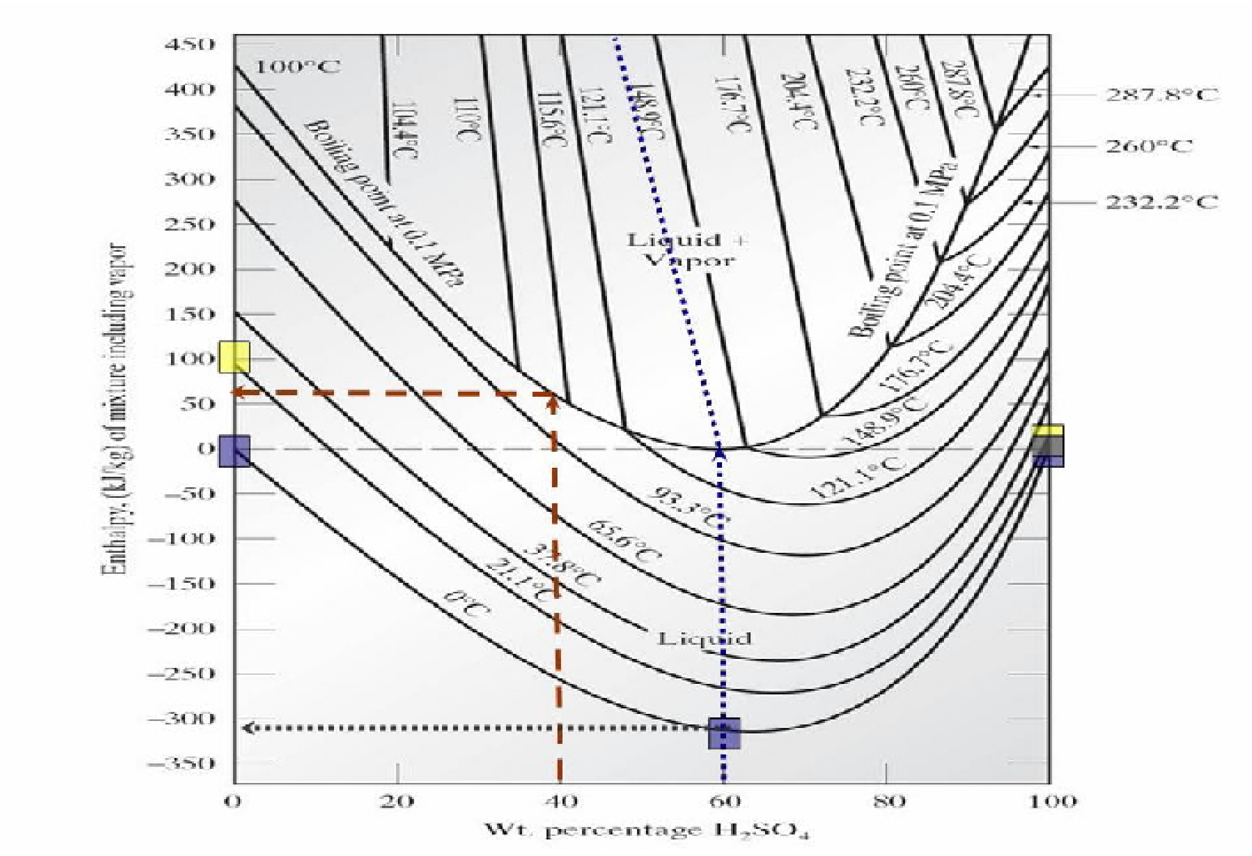
c) The heat of mixing requires knowing the actual enthalpy as well as the pure component enthalpies, taking into consideration that the pressure is kept fixed all the time at 1 atm.

$$\begin{aligned} h_{H_2SO_4}(x &= 1.0, T = 0°\text{C}) \simeq 0 \text{ kJ/kg} \\ h_{H_2O}(x &= 1.0, T = 0°\text{C}) \simeq 0 \text{ kJ/kg} \\ h(x &= 0.6, T = 0°\text{C}) \simeq -315 \text{ kJ/kg} \end{aligned}$$

The heat of mixing is defined as

$$\begin{aligned} \Delta h_{\text{mix}} &= h(T, P, \mathbf{x}) - \sum x_i h_i(T, P) \\ &= -315 - (0.6)(0) - (0.4)(0) = -315 \text{ kJ/kg.} \end{aligned}$$

Which indicates that this mixing process is exothermic which is accompanied by release of energy.



450
400
350
300
250
200
150
100
50
0
−50
−100
−150
−200
−250
−300
−350
Enthalpy, (kJ/kg) of mixture including vapor
0
20
40
60
80
100
Wt. percentage H_2SO_4
100°C
104.4°C
110°C
115.6°C
121.1°C
148.9°C
176.7°C
204.4°C
232.2°C
260°C
287.8°C
Boiling point at 0.1 MPa
Liquid + Vapor
Boiling point at 0.1 MPa
204.4°C
176.7°C
148.9°C
121.1°C
93.3°C
65.6°C
37.8°C
21.1°C
0°C
Liquid
287.8°C
260°C
232.2°C

Lower and higher explosion limits of nonane

a) Maximum mole fraction of nonane achieved if all the liquid evaporates and none escapes.

$$n_{\max} = 15(0.718)/128.25 = 0.0084 \text{ kmol } C_9H_{20}.$$

Assume $P = 1$ atm, and $T = 25°\text{C}$. The number of moles of gas, assumed to be air, in the tank is given by

$$\begin{aligned} n_{\text{gas}} &= \frac{PV}{RT} = \frac{(101325)(20)}{(8.314)(298.15)} = 817.53 \text{ mole} \\ y_{\max} &= \frac{n_{\max}}{n_{\text{gas}}} = \frac{0.0084}{0.81753} = 1.0275 \times 10^{-2} \end{aligned}$$

As the nonane evaporates, the mole fraction will pass through the explosive range (0.8% to 2.9%). The answer is therefore $\boxed{\text{YES}}$.The nonane will not spread uniformly—it will be high near the sump as long as liquid is present (and low far from the sump). There will always be a region where the mixture is explosive at some time during the evaporation.

b)

$$\begin{aligned} \ln P^* &= -\frac{A}{T} + B \\ -A &= \frac{\ln \frac{40}{5}}{\frac{1}{339} - \frac{1}{299}} \rightarrow A = 5269 \\ B &= \ln(5) + \frac{5269}{299} = 19.23 \\ P^* &= \exp\left[19.23 - \frac{5269}{T}\right] \end{aligned}$$

At lower explosion limit,

$$\begin{aligned} y &= 0.008 \text{ mol } C_9H_{20}/\text{mol} \\ P^* &= yP = 0.008(760) = 6.08 \text{ mm Hg} \end{aligned}$$

Solve for the temperature as

$$T = \frac{A}{B - \ln P^*} = \frac{5269}{19.23 - \ln(6.08)} = 302.4 \text{ K}$$

c) The purpose of purge is to evaporate and carry out the liquid nonane. Using steam rather than air is to make sure an explosive mixture of nonane and oxygen is never present in the tank. Before anyone goes into the tank, a sample of the contents should be drawn and analyzed for nonane.