Chapter 7 Assignment  
(Answers are in parenthesis)

VLE by Raoult’s Law

1. Assuming the validity of Raoult’s law, do the following calculations for the benzene(1)/toluene(2) system: (a) Given $x_1 = 0.33$ and $T = 100\,^\circ C$, find $y_1$ and $P$ ($P= 109.12\,kPa$, $y_1 = 0.545$) 
(b) Given $y_1 = 0.33$ and $T = 100\,^\circ C$, find $x_1$ and $P$ ($T= 92.04\,kPa$, $x_1 = 0.169$)  
(c) Given $x_1 = 0.33$ and $P= 120\,kPa$, find $y_1$ and $T$ ($T= 103.4\,^\circ C$, $y_1 = 0.542$) 
(d) Given $y_1 = 0.33$ and $P = 120\,kPa$, find $x_1$ and $T$. ($T= 109.16\,^\circ C$, $x_1 = 0.173$) 
(e) Given $T = 105\,^\circ C$ and $P = 120\,kPa$, find $x_1$ and $y_1$ [$x_1 = 0.33$, $y_1 = 0.485$]  
(f) For part (e) if the overall mole fraction of benzene is $z_1=0.3685$, what molar fraction of the system is vapour? [$V=0.231$]

2. Assuming Raoult’s law to apply to the system n-pentane(1)/n-heptane(2). (a) What are the values of $x_1$ and $y_1$ at $T = 55\,^\circ C$ and $P=\frac{1}{2}\left(p_{1}^{sat} + p_{2}^{sat}\right)$? [$x_1 = 0.5$, $y_1 = 0.915$] 
(b) If we plot vapor molar fraction $V$ vs. overall composition $z_1$, is the plot linear / non-linear? [Linear] 
(c) For $T = 55\,^\circ C$ and $z_1 = 0.5$, If $V = 0.5$ find: $P$, $x_1$, and $y_1$. [Approximate values are $P ~ 50kPa$, $x_1 ~ 0.2$ and $y_1 = 0.8$]

3. A single-stage liquid/vapor separation for the benzene(1)/ethylbenzene(2) system must produce phases of the following equilibrium compositions. For $x_1 = 0.35$, $y_1 = 0.70$, determine the $T$ and $P$ in the separator. What additional information is needed to compute the relative molar amounts of liquid and vapor leaving the separator? Assume that Raoult’s law applies. [$T=134\,^\circ C$, $P=207\,kPa$, need $z_i$]

4. A liquid mixture containing equimolar amounts of benzene(1)/toluene(2) and ethylbenzene(3) is flashed to conditions $T$ and $P$. For $T = 110\,^\circ C$, $P = 90 \,kPa$, determine the equilibrium mole fractions $\{x_i\}$ and $\{y_i\}$ of the liquid and vapor phase formed and the molar fraction $V$ of the vapor formed. Assume that Raoult’s law applies. [$V=0.834$, $x_1 = 0.143$, $y_1 = 0.371$, $x_2 = 0.306$, $y_1 = 0.339$].

5. A liquid mixture of 25mol% pentane(1), 45mol% hexane(2) and 30mol% heptane(3) initially at high pressure and $69\,^\circ C$ is partially vaporized by isothermally lowering the pressure to 1atm. Find the relative amounts of liquid and vapour in the system and the compositions. [$L=0.564$, $x_1 = 0.142$, $x_2 = 0.448$, $y_1= 0.390$, $y_2= 0.453$] The vapour pressure relations are $\{\ln P_i^s\,(bar);(\theta K)\}$: $\ln P_1^s = 10.422 - 26799/RT$; $\ln P_2^s = 10.456 - 29676/RT$; $\ln P_3^s = 11.431 - 35200/RT$
Non-ideal System VLE

6. For the system ethyl ethanoate(1)/n-heptane(2) at 70°C, \( \ln \gamma_1 = 0.95 x_2^2; \ln \gamma_2 = 0.95 x_1^2; \) \( p_1^{\text{sat}} = 79.80 \text{ kPa}; \) \( p_2^{\text{sat}} = 40.50 \text{ kPa}, \) (a) Make a BUBL P calculation for \( T = 70^\circ\text{C}, x_1 = 0.05. \) \[ P = 47.97 \text{ kPa}, y_1 = 0.196 \] (b) Make a DEW P calculation for \( T = 70^\circ\text{C}, y_1 = 0.05. \) \[ P = 42.19 \text{ kPa}, x_1 = 0.0104 \], (c) What is the azeotrope composition and pressure at \( T = 70^\circ\text{C}? \) \[ P_{\text{az}} = 47.97 \text{ kPa}, x_1^{\text{az}} = y_1^{\text{az}} = 0.857 \]

7. A liquid mixture of cyclohexanone(1)/phenol(2) for which \( x_1 = 0.6 \) is in equilibrium with its vapor at 144°C. Determine the equilibrium pressure \( P \) and vapor composition \( y_1 \) from the following information: \( \ln \gamma_1 = A x_2^2; \ln \gamma_2 = A x_1^2 \) At 417.15 K (144°C), \( P_1^{\text{sat}} = 75.20 \) and \( P_2^{\text{sat}} = 31.66 \text{ kPa}. \) The system forms an azeotrope at 417.15 K (144°C) for which \( x_1^{\text{az}} = y_1^{\text{az}} = 0.294. \) \[ P = 38.19 \text{ kPa}, y_1 = 0.844 \]

8. For the acetone (1)/methanol (2) system a vapor mixture for which \( z_1 = 0.25 \) is cooled to temperature \( T \) in the two-phase region and flows into a separation chamber at a pressure of 1 bar. If the composition of the liquid product is to be \( x_1 = 0.175, \) what is the required value of \( T, \) and what is the value of \( y_1? \) For liquid mixtures of this system to a good approximation: \( \ln \gamma_1 = 0.64 x_2^2; \ln \gamma_2 = 0.64 x_1^2 \) \[ T = 59.4^\circ\text{C}, y_1 = 0.307 \]

9. The following is a rule of thumb: For a binary system in VLE at low pressure, the equilibrium vapor-phase mole fraction \( y_1 \) corresponding to an \textit{equimolar} liquid mixture is approximately \( \gamma_1 = P_1^{\text{sat}} / (P_1^{\text{sat}} + P_2^{\text{sat}}); \) where \( P_i^{\text{sat}} \) is a pure-species vapor pressure. Clearly, this equation is valid if Raoult’s law applies. Prove that it is also valid for VLE described by with: \( \ln \gamma_1 = A x_2^2 \) and \( \ln \gamma_2 = A x_1^2 \)

10. For a distillation column separating ethyl-ether(1)/ ethanol(2) into essentially pure components at 1atm, find the range of values of \( \alpha_{12} \) (relative volatility).

\textbf{Data}: \( \ln P_1^s = 9.25-2420.72 \) / (T-45.72), \( \ln P_2^s = 12.17 - 3737.60 / (T-44.17), \) where \( P \) (bar), \( T(K), \) For the liquid phase, \( G^E / x_1 x_2 RT = A_{21} x_1 + A_{12} x_2, \) \( A_{12} = 0.1665+233.74/T; A_{21} = 0.5908+197.55/T. \)

\[ \alpha_{12}(x_1 \rightarrow 1) = 2.2, \alpha_{12}(x_2 \rightarrow 1) = 8.64 \]
11. Find if Benzene(1)/Cyclohexane(2) forms an azeotrope at 77.6°C. The following data are available for use of Regular Solution theory. At 77.6°C, $P_1^s = 745 \text{ mm Hg}$, $P_2^s = 735 \text{ mm Hg}$. $[(x_1)^{az} = 0.525]$

<table>
<thead>
<tr>
<th>Species(i)</th>
<th>$V_i$(cc/mole)</th>
<th>$\delta_i$(cal/cc)$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>89</td>
<td>9.2</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>109</td>
<td>8.2</td>
</tr>
</tbody>
</table>

**High Pressure VLE and Henry’s Law**

12. A vapour mixture contains 20mol% methane, 30mol% ethane, and rest propane, at 30°C. Determine the dew composition. $[x_1 = 0.0247, x_2 = 0.1648]$  

13. A liquid mixture of 50mol% pentane and 50mol% heptane initially at low temperature is heated at a constant pressure of 1 atm until 50mol% of the liquid is vapourized. Calculate the relevant compositions and the temperature. $[x_1=0.274, y_1=0.726, T = 341.7^0K]$  

14. A vapor mixture of 40 mole percent ethylene and 60 mole percent propylene at 40C and 500 kPa is isothermally compressed. Determine the pressure at which condensation begins and the composition of the first drop of liquid that forms. $[2.65\text{MPa}]$  

15. A liquid mixture of 25 mole percent ethylene and 75 mole percent propylene at -40C is kept in a piston-cylinder assembly. The piston exerts a constant pressure of 1 MPa. Compute the bubble temperature and composition. $[-8.5^0C]$  

16. A system formed of methane (1) and a light oil(2) at 200 K and 30 bar consists of a vapour phase containing 95 mol- % methane and a liquid phase containing oil and dissolved methane. The fugacity of the methane is given by Henry’s law, and at the temperature of interest Henry’s constant is $H_1 = 200 \text{ bar}$. Assuming **ideal solution** in gas phase estimate the equilibrium mole fraction of methane in the liquid phase. Use virial EOS for gas phase. $[0.118]$  

17. Using PR-EOS: Compute the dew pressure for methane (1) / butane (2) system at 310K with $y_1=0.80$ $[\text{Dew P}=23.6 \text{ bar}, x_1=0.1094]$