CHAP. 10

INTRODUCTION TO VAPOR/LIQUID EQUILIBRIUM.

⇒ THERMODYNAMICS OF SEPARATIONS

BEFORE:

\[
\begin{array}{c}
\alpha \\
\beta
\end{array}
\]

Two phases \(\alpha + \beta\)

Composition of \(\alpha + \beta\) same

(one component)

WHAT ABOUT MULTIPLE COMPONENT SYSTEMS?

NOW:

\[
\begin{array}{c}
\alpha \\
\beta
\end{array}
\]

Two phases \(\alpha + \beta\)

Composition of \(\alpha + \beta\) different

\(y_\alpha \neq x_\beta\)

\[\text{Note: } T_\alpha = T_\beta, \ p_\alpha = p_\beta\]
Expressions for composition:

**Vapor Phase:**

\[ y_i \] (mole or mass fraction)

\[ P_i \] (partial pressure)

\[ n_i \] (moles component \( i \))

\[ m_i \] (mass component \( i \))

\[ M = \text{total mass of vapor phase} \]

\[ n = \text{total moles of vapor phase} \]

\[ y_i = \frac{n_i}{n} \quad \text{mole fraction} \]

\[ y_i = \frac{m_i}{M} \quad \text{mass fraction} \]

**Gas Phase**

\[ \Rightarrow \]

Beware: \( \frac{n_i}{n} \neq \frac{m_i}{M} \)

\[ \Rightarrow \text{Make sure to check if mass or moles.} \]
Nice thing about mass and mole fractions:

\[ \sum_i \frac{n_i}{n} = 1 \quad \text{and} \quad 0 \leq \frac{n_i}{n} \leq 1 \]

\[ \sum_i \frac{M_i}{m} = 1 \quad \text{and} \quad 0 \leq \frac{M_i}{m} \leq 1 \]

Finally, Partial Pressure...

\[ P_i = y_i \cdot P \quad \text{Total Pressure.} \]

↓ mole fraction of component "i".

AND

\[ \sum_i P_i = P \]

How about liquid phase?

\[ \chi_i = \frac{n_i}{n} \quad \text{mole fraction} \]

\[ \chi_i = \frac{M_i}{m} \quad \text{mass fraction} \]
**Beware:** \( \frac{n_i}{n} \neq \frac{m_i}{m} \)

**Also:** \( \sum_i x_i = 1 \) and \( 0 \leq x_i \leq 1 \)

**Finally:** Concentration

If mass:

\[ C_i = \frac{m_i}{V} \quad \text{[=]} \quad \frac{\text{mass}}{\text{volume}} \quad (\text{units of } \rho) \]

If moles:

\[ C_i = \frac{n_i}{V} \quad \text{[=]} \quad \frac{\text{mol}}{\text{volume}} \quad (\text{units of molar } \rho) \]

In both cases,

\[ \sum_i C_i = C_T \quad \text{total concentration} \]

And,

\[ M = \sum_i x_i M_i \quad \text{Molar mass of a solution} \]
10.2 THE PHASE RULE: DUHSM'S THEOREM

1) Compositions are intensive \((y_i, x_i, p_i, c_i)\) and extensive \((n_i, m_i)\).

The intensive variable obey the phase rule.

2) Example:

\[ F = 2 - T + N \]

If \( F = 2 + T + P \) specified,

then \( c_i, x_i, y_i, p_i \) also set.

10.4 SIMPLE MODELS FOR VLE

We already know \( y_i \neq x_i \) for mixtures. (most cases)

When is this \( y_i = x_i \) the case?
However, \[ y_i \propto x_i \]

or

\[ y_i = K_i x_i \]

Proportionality constant.

How to get \( K_i \)?

Two simple models.

**Raoult's Law**:

\[ y_i p_i = x_i p_i^{3x+} \quad (i = 1, 2, \ldots, N) \]

\[ \Rightarrow K_i = \frac{p_i^{3x+}}{p} \]

Assumptions:
1) Ideal gas
2) Ideal liquid

\[ \Rightarrow \text{no interactions} \]
 ASK YOURSELF 2 QUESTIONS.

1) IS THE GAS PHASE IDEAL?
   -> LOW TO MODERATE PRESSURE
   -> LARGE VOLUME

2) IS THE LIQUID PHASE IDEAL?
   -> ANY SPECIFIC INTERACTIONS?
   a) H-Bonding
   b) Pi-Pi: Stacking
   c) Electrostatic
   d) Polar molecules
   e) BIG DIFFERENCES BETWEEN MOLECULES IN SOLUTION.

GOOD EXAMPLE IDEAL SOLUTION;
ALKANES / MIXTURES OF AROMATICS

WHEN NON-IDEAL?
WATER + OTHER H-BONDING MOLECULES
BACK TO RAOULT'S LAW:

\[ Y_i \cdot P = X_i \cdot P_i^{\text{sat}} \]

\( Y_i \) mole fraction vapor
\( X_i \) mole fraction liquid
\( P \) total pressure
\( P_i^{\text{sat}} \) vapor pressure pure Component "i"

(Vapor Pressure Pure Component "i" = \( f(T) \) only)

(Antoine Eqn.)

\( \Rightarrow \text{Lots of limitations, but not bad for most things as } X_i \to 1. \)

Dewpoint + Bubblepoint Calculations w/ Raoult's Law:

First, WHAT IS A DEWPOINT?

\( \alpha \) \( \beta \)

\( \alpha \) \( \beta \)

\( \alpha \) = Vapor Phase
\( \beta \) = Liquid Phase

Dewpoint: Last drop of liquid vaporized
First drop of liquid condensed.
Practically: \[ V = F \]
\[ L = 0 \]

where \( V \) = Volume for Vapor Phase
\( L \) = Volume of Liquid Phase
\( F \) = Total Volume.

Next, what is a Bubble Point?

\[ \alpha \] = Vapor Phase
\[ \beta \] = Liquid Phase

Bubble point: First bubble of vapor formed

or

Last bubble of vapor condensed.

So, what are Dew Point and Bubble Point calculations?

From Phase Rule:

\[ F = 2 - \Pi + N \]
IF $2 \equiv$ COMPOUND + 1 PHASE
(RECALL @ DEW POINT $V = F + L = 0$)

$\Rightarrow$ $F = 2 - 1 + 2 = 3$

$\Rightarrow$ SPECIFY 3 PARAMETERS + ALL OTHER
INTENSIVE VARIABLES ARE FIXED.

WHAT VARIABLES?

$x_i, y_i, p, T$, where $i = 1 + 2$

$\Rightarrow$ $x_1, y_2, y_1, y_2, p, T \Rightarrow 6$ variables

4 CASES:

1. BUBBLE P:

$\Rightarrow$ WANT COMPOSITION OF FIRST BUBBLE
+ WANT P.

$\Rightarrow$ HAVE SPECIFIED $x_1, x_2, T$. 
2) **DEW P**

Want: \( x_1, x_2, P \)

Have: \( y_1, y_2, T \)

3) **BUBBLE T**

Want: \( y_1, y_2, T \)

Have: \( x_1, x_2, P \)

4) **DEW T**

Want: \( x_1, x_2, T \)

Have: \( y_1, y_2, P \)

Recall: \( y_i P = x_i P_i^{sat} \) (RAOUlT'S LAW)

Write FOR EACH component:

\[ y_1 P = x_1 P_1^{sat} \]

\[ + y_2 P = x_2 P_2^{sat} \]

\[ P(y_1,y_2) = x_1 P_1^{sat} + x_2 P_2^{sat} \]
\[ P = x_1 p_1^{\text{sat}} + x_2 p_2^{\text{sat}} \]

But \( \sum_i x_i = 1 \Rightarrow x_1 + x_2 = 1 \)

Substitute for \( x_2 \)

\[
P = x_1 p_1^{\text{sat}} + (1 - x_1) p_2^{\text{sat}}
\]

\[
P = p_2^{\text{sat}} + x_1 (p_1^{\text{sat}} - p_2^{\text{sat}})
\]

\[
\hat{P} = \frac{1}{\sum_i \left( \frac{y_i}{p_i^{\text{sat}}} \right)}
\]

**Note:**

\[ \text{p}^{\text{sat}} \text{ by Antoine equation} \]

\[ \Rightarrow \text{Phase Diagrams for Ideal Gas} \]

\[ \neq \text{Ideal Liquid} \]

(See Attached Flow Charts.)

(In Class Exercise)
PX Y (IDEAL GAS/IDEAL LIQUID)

- Raoult's Law Applies
- Antoine Eqn. for $p_i^{sat}$
- Constant $T$

1. Calculate $p_1^{sat} + p_2^{sat}$

2. Pick $x_1$

3. Calculate $P = p_2^{sat} + (p_1^{sat} - p_2^{sat})x_1$

4. Calculate $y_1 = \frac{x_1 p_i^{sat}}{P}$

5. **No**
   - Across $x_1$ Range?
     - **Yes**
       - Plot $PX Y$ Diagram
     - Plot $XY$ Diagram
TXY (Ideal Gas/Ideal Liquid)

- Raoult's Law Applies
- Antoine Equation for $p_i^{sat}$
- Constant $P$

From $p_i$, calculate $T_i^{sat} + T_2^{sat}$

Pick $T$

Calculate $p_1^{sat} + p_2^{sat}$

Calculate $x_1$:

$$x_1 = \frac{p - p_2^{sat}}{p_1^{sat} - p_2^{sat}}$$

Calculate $y_1$:

$$y_1 = \frac{x_1 p_i^{sat}}{p}$$

Access $T$ range?

No

Yes

Plot TXY Diagram

Plot XY Diagram
WHAT TO DO IF \( T > T_c \)?

(No \( P_{c, sat} \))

\[ y_i \rho = x_i \bar{H}_i \]

\( \bar{H}_i \) - Henry's Law Constant

Values of \( \bar{H}_i \) in Table 10.1 (p. 357)

**Example 10.2**

Assuming that carbonated water contains only \( CO_2(1) \) and \( H_2O(2) \), determine the compositions of the vapor and liquid phases in a sealed can of soda and the pressure exerted on the can at 10°C. Henry's Law constant for \( CO_2 \) in water at 10°C is about 990 bar.

**Given:** \( x_{CO_2} = 0.01 \).

**Phase Rule:** \( F = 2 - 2 + 2 = 2 \)

**Given:** \( T = 283 \text{ K} \)

\( x_{CO_2} = 0.01 \)  \( \Rightarrow \) All other intensive variables set.
\[
\text{CO}_2: \quad y_{\text{CO}_2} \cdot P = x_{\text{CO}_2} \cdot P_{\text{CO}_2} \\
\text{H}_2\text{O}: \quad y_{\text{H}_2\text{O}} \cdot P = x_{\text{H}_2\text{O}} \cdot P_{\text{H}_2\text{O}}
\]

\[
P(y_{\text{CO}_2} + y_{\text{H}_2\text{O}}) = x_{\text{CO}_2} \cdot P_{\text{CO}_2} + x_{\text{H}_2\text{O}} \cdot P_{\text{H}_2\text{O}}
\]

\[
= 1
\]

\[
x_{\text{CO}_2} = 0.01 \quad \Rightarrow \quad x_{\text{H}_2\text{O}} = 0.99
\]

\[
P_{\text{CO}_2} = 990 \text{ bar (given)}
\]

\[
P_{\text{H}_2\text{O}} \text{ (steam table at } 10^\circ\text{C)} = 1.227 \text{ kbar}
\]

\[
= 0.01227 \text{ bar}
\]

⇒ Plug + Chug

\[
P = (0.01)(990 \text{ bar}) + (0.99)(0.01227 \text{ bar})
\]

\[
P = 9.912 \text{ bar}
\]
\[ y_{\text{CO}_2} = \frac{x_{\text{CO}_2} \cdot P_{\text{CO}_2}}{P} \]

\[ = \frac{(0.01)(970 \text{ bar})}{9.912 \text{ bar}} \]

\[ y_{\text{CO}_2} = 0.9988 \]

\[ \Rightarrow y_{\text{H}_2\text{O}} = 1 - 0.9988 = 0.0012 = y_{\text{H}_2\text{O}} \]

Check: \[ y_{\text{H}_2\text{O}} = \frac{(0.79)(0.01227)}{9.912} = 0.0012 \]

Next time: Modified Raoult's Law

(liquid goes non ideal)
VLE by Modified Raoult's Law.

10.5

Low to Moderate Pressure

Non-Ideal Liquid.

\[ y_i \rho = x_i \gamma_i \rho_i^{sat} \]

Activity Coefficient

\[ K_i = \frac{x_i \rho_i^{sat}}{\rho} \]

\[ \rho = \sum_i x_i y_i \rho_i^{sat} \]

or

\[ \rho = \frac{1}{\sum_i \left( \frac{y_i}{x_i \rho_i^{sat}} \right)} \]
From Activity Coefficient Model

Simple: (Polynomial)
Margules - 2 Suffix
Van Laar
Margules - 3 Suffix

Local Composition:
Wilson
NRTL

Group Contribution:
UNIFAC
UNIQUEAL

Details in Chap. 12
For the system methanol (1) / methyl acetate (2), the following equations provide a reasonable correlation for the activity coefficients:

\[ \ln \gamma_1 = A x_2^2 \]
\[ \ln \gamma_2 = A x_1^2 \]

where \( A = 2.771 - 0.00523T \)

\[ \ln p_{1\text{sat}} = 16.59158 - \frac{3.643.31}{T - 33.424} \]

\[ \ln p_{2\text{sat}} = 14.25326 - \frac{2.665.54}{T - 53.424} \]

where \( T \) is in K and \( p \) is in kPa.

(a) Calculate \( p \) and \( y_1 \) for \( T = 318.15 \text{ K} \) and \( x_1 = 0.25 \)

(b) Calculate \( p \) and \( x_2 \) for \( T = 318.15 \text{ K} \) and \( y_1 = 0.60 \)

(c) Calculate \( T \) and \( y_1 \) for \( p = 101.33 \text{ kPa} \) and \( x_1 = 0.85 \)

(d) Calculate \( T \) and \( x_1 \) for \( p = 101.33 \text{ kPa} \) and \( y_1 = 0.40 \)
(a) Calculate \( P \) and \( y_i \): with \( T = 318.15 \text{K} \) and \( x_i = 0.25 \)

\[ x_2 = 0.75 \]

\[ A = 2.771 - 0.00523(318.15) = 1.1071 \]

\[ \ln x_1 = 1.1071 \cdot x_2 \Rightarrow x_1 = 1.8640 \]

\[ \ln x_2 = 1.1071 \cdot x_1 \Rightarrow x_2 = 1.0716 \]

\[ P_{1,\text{sat}} = \exp \left\{ \frac{16.59158 - \frac{3.643.31}{318.15 - 33.424}}{318.15 - 33.424} \right\} = 44.51 \text{ kPa} \]

\[ P_{2,\text{sat}} = \exp \left\{ \frac{14.25326 - \frac{2.665.54}{318.15 - 53.424}}{318.15 - 53.424} \right\} = 65.64 \text{ kPa} \]

\[ P = (0.25)(1.8640)(44.51 \text{ kPa}) + (0.75)(1.0716)(65.64 \text{ kPa}) \]

\[ P = 73.5 \text{ kPa} \]

\[ y_1 = x_1, \quad \frac{P_{1,\text{sat}}}{P} = \frac{(0.25)(1.8640)(44.71 \text{ kPa})}{(73.5 \text{ kPa})} = 0.282 = y_1 \]

\[ y_2 = 1 - y_1 = 0.718 = y_2 \]
(b) Calculate $P + Y_i$ for $T = 318.15$ K

$Y_i = f(Y_i) \Rightarrow$ PROBLEM (Need to iterate)

\[ Y_i = 0.60 \Rightarrow Y_2 = 0.40 \]

**Procedure:**

1) Guess Values for $X_i$
2) Calculate $P$
3) Calculate $X_i$
4) Calculate $Y_i$
5) Repeat Steps 2-4 until no change in $X_i$

**Equations:**

\[
P = \frac{1}{\sum_{i=1}^{4} \left( \frac{Y_i}{X_i P + P} \right)}
\]

\[
P = \frac{1}{\frac{0.6}{44.51 X_1} + \frac{0.4}{65.64 X_2}}
\]

\[
X_1 = \frac{0.6 P}{44.51 X_1}
\]

\[
X_2 = 1 - X_1
\]

\[
Y_1 = \exp \left\{ 1.1071 X_2^2 \right\}
\]

\[
Y_2 = \exp \left\{ 1.1071 X_1^2 \right\}
\]
<table>
<thead>
<tr>
<th>( \gamma_1 )</th>
<th>( \gamma_2 )</th>
<th>( P )</th>
<th>( x_1 )</th>
<th>( x_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>51.09</td>
<td>0.689</td>
<td>0.311</td>
</tr>
<tr>
<td>1.113</td>
<td>1.691</td>
<td>63.63</td>
<td>0.771</td>
<td>0.229</td>
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<tr>
<td>1.060</td>
<td>1.931</td>
<td>63.00</td>
<td>0.801</td>
<td>0.199</td>
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<tr>
<td>1.045</td>
<td>2.035</td>
<td>62.90</td>
<td>0.811</td>
<td>0.187</td>
</tr>
<tr>
<td>1.040</td>
<td>2.071</td>
<td>62.88</td>
<td>0.815</td>
<td>0.185</td>
</tr>
<tr>
<td>1.037</td>
<td>2.086</td>
<td>62.91</td>
<td>0.816</td>
<td>0.184</td>
</tr>
<tr>
<td>1.038</td>
<td>2.090</td>
<td>62.88</td>
<td>0.817</td>
<td>0.183</td>
</tr>
</tbody>
</table>

Pretty good.

\[ P = 62.88 \text{ kPa} \]
\[ x_1 = 0.817 \]
\[ x_2 = 0.183 \]

(c) Calculate \( T + \gamma_i \): Given \( P = 101.33 \text{ kPa}, x_1 = 0.85 \)

\( \gamma_i = f(T) \): Problem. (Iterative Procedure)

Procedure:
1) Guess \( T \)
2) Calculate \( A \)
3) Calculate \( \gamma_i \)
4) Calculate \( P_{\text{set}} \)
5) Calculate \( P \) (\( P = 101.33 \text{ kPa} \)?)

Initial Based on Weighted \( T \)
<table>
<thead>
<tr>
<th>$T$</th>
<th>$A$</th>
<th>$\delta_1$</th>
<th>$\delta_2$</th>
<th>$P_1$</th>
<th>$P_2$</th>
<th>$t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>330.6</td>
<td>1.01</td>
<td>1.023</td>
<td>2.074</td>
<td>76.77</td>
<td>120.50</td>
<td>128.7</td>
</tr>
<tr>
<td>331.0</td>
<td>1.04</td>
<td>1.024</td>
<td>2.120</td>
<td>77.35</td>
<td>104.62</td>
<td>100.6</td>
</tr>
<tr>
<td>331.1</td>
<td>1.039</td>
<td>1.024</td>
<td>2.118</td>
<td>77.16</td>
<td>104.98</td>
<td>100.9</td>
</tr>
<tr>
<td>331.2</td>
<td>1.039</td>
<td>1.024</td>
<td>2.118</td>
<td>77.98</td>
<td>105.35</td>
<td>106.3</td>
</tr>
</tbody>
</table>

\begin{align*} 
T_1^{Sat} &= \frac{3.643.31}{16.9158 - \ln(101.33)} + 33.424 = 337.7 \text{ K} \\
T_2^{Sat} &= \frac{2.645.54}{14.25326 - \ln(101.33)} + 53.424 = 330.1 \text{ K} 
\end{align*}

Initial Guess $T = 0.85(339.7) + 0.15(336.1) = 336.6 \text{ K}$

\begin{align*} 
&\Rightarrow T = 336.2 \text{ K} \\
y_1 = \frac{(0.85)(1024)(77.98 \text{ kK})}{(101.3 \text{ kK})} = 0.67 = y_1 \\
y_2 = 1 - 0.67 \Rightarrow y_2 = 0.33 
\end{align*}
(d) Calculate $T$ + $x_i$  
Given $P = 101.33$ kPa + $y_i = 0.40$

$T_1 = 337.7\,\text{K} \quad T_2 = 330.1\,\text{K}$

Initial Guess: $T = 0.4(337.7) + (0.6)(330.1)$

$T = 333.1\,\text{K}$

Don't know $x_i$ => Assume $x_i = 1$ (Guess)

**Procedure:**
1) Evaluate $A_i$, $P_i^{sat}$  
   Guess New $T$
2) Calculate $x_i$
3) Calculate $\delta_i$
4) Calculate $P$

$T = 333.1\,\text{K} + \delta_i = 1$, $x_2 = 1$

$\Rightarrow A = 1.029$

$\Rightarrow P_1^{sat} = 84.27\,\text{kPa} \quad P_2^{sat} = 112.44\,\text{kPa}$

$\Rightarrow x_1 = 0.481 \quad x_2 = 0.519$

$\Rightarrow \delta_1 = 1.319 \quad \delta_2 = 1.269$

$\Rightarrow P = 127.52\,\text{kPa} \neq 101.33\,\text{kPa}$

(Lower $T$)
\[ T = 328 \text{ K} \quad \delta_1 = 1.319 \quad \delta_2 = 1.269 \]

\[ \Rightarrow A = 1.056 \]

\[ \Rightarrow p_1^{\text{sat}} = 68.28 \text{ kPa} \quad p_2^{\text{sat}} = 94.20 \text{ kPa} \]

\[ \Rightarrow x_1 = 0.450 \quad x_2 = 0.550 \]

\[ \Rightarrow \delta_1 = 1.376 \quad \delta_2 = 1.238 \]

\[ \Rightarrow P = 104.42 \text{ kPa} \neq 101.33 \text{ kPa} \quad (\text{Lower } T) \]

\[ T = 327 \text{ K} \quad \delta_1 = 1.376 \quad \delta_2 = 1.269 \]

\[ \Rightarrow A = 1.061 \]

\[ \Rightarrow p_1^{\text{sat}} = 65.46 \text{ kPa} \quad p_2^{\text{sat}} = 90.72 \text{ kPa} \]

\[ \Rightarrow x_1 = 0.450 \quad x_2 = 0.550 \]

\[ \Rightarrow \delta_1 = 1.378 \quad \delta_2 = 1.240 \]

\[ \Rightarrow P = 102.60 \text{ kPa} \neq 101.33 \text{ kPa} \quad (\text{Lower } T) \]
\[ T = 326 \text{ K} \quad \delta_1 = 1.378 \quad \delta_2 = 1.240 \]

\[ \Rightarrow A = 1.066 \]

\[ \Rightarrow p_{1, \text{sat}} = 4.274 \text{ kPa} \]

\[ \Rightarrow x_1 = 0.469 \]

\[ \Rightarrow y_1 = 1.351 \]

\[ \Rightarrow P = 98.63 \text{ kPa} \neq 101.3 \text{ kPa} \]

\[ \text{(Increase T)} \]

\[ T = 326.7 \text{ K} \quad \delta_1 = 1.351 \quad \delta_2 = 1.264 \]

\[ \Rightarrow A = 1.062 \]

\[ \Rightarrow p_{1, \text{sat}} = 64.64 \text{ kPa} \]

\[ \Rightarrow x_1 = 0.464 \quad x_2 = 0.536 \]

\[ \Rightarrow y_1 = 1.357 \quad y_2 = 1.257 \]

\[ \boxed{P = 101.3 \text{ kPa}} \]

\[ \Rightarrow \begin{cases} x_1 = 0.464 \\ x_2 = 0.536 \end{cases} \]
VLE FROM K-VALUE CORRELATIONS

\[ K_i = \frac{y_i}{x_i} \]

\[ K_i \text{ from Raoult's Law or Modified Raoult's Law.} \]

\[ K_i = \frac{p_i \text{ sat}}{P} \quad \text{RAOUlt'S LAW} \]

(IDEAL GAS/IDEAL LIQUID)

\[ K_i = \frac{y_i p_i \text{ sat}}{P} \quad \text{MODIFIED RAOUlt'S LAW} \]

(IDEAL GAS/NON-IDEAL LIQUID)

DePriester CHARTS (BASED ON RAOUlt'S LAW)

(Fig. 10.13 & 10.14)

WHY? \[ K_i = f(T, P) \text{ only.} \]

(for RAOUlt'S LAW)
**Example 10.4** For a mixture of 10 mol% CH₄, 20 mol% C₂H₆, and 70 mol% C₃H₈ @ 50°F,
Determine:
(a) Dewpoint Pressure
(b) Bubblepoint Pressure

K-values are given in Figure 10.13.

(a) Dewpoint

⇒ Essentially all vapor

⇒ Overall composition \( \approx y_i \)

<table>
<thead>
<tr>
<th>Species</th>
<th>( y_i )</th>
<th>( K_i )</th>
<th>( \frac{y_i}{K_i} )</th>
<th>( K_i )</th>
<th>( \frac{y_i}{K_i} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0.1</td>
<td>20</td>
<td>0.005</td>
<td>13.3</td>
<td>0.008</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.2</td>
<td>3.2</td>
<td>0.063</td>
<td>2.2</td>
<td>0.091</td>
</tr>
<tr>
<td>Propane</td>
<td>0.7</td>
<td>0.92</td>
<td>0.761</td>
<td>0.66</td>
<td>1.061</td>
</tr>
</tbody>
</table>

\[
\sum_i x_i = \sum_i \frac{y_i}{K_i} = 1
\]

Higher P

Lower P
From linear interpolation, guess \( P \approx 126 \) psi.

<table>
<thead>
<tr>
<th>Species</th>
<th>( \frac{y_i}{K_i} )</th>
<th>( g_i/K_i )</th>
<th>( \frac{y_i}{K_i} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0.1</td>
<td>16</td>
<td>0.006</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.2</td>
<td>2.7</td>
<td>0.074</td>
</tr>
<tr>
<td>Propane</td>
<td>0.7</td>
<td>0.78</td>
<td>0.897</td>
</tr>
</tbody>
</table>

\[
\frac{0.977}{\text{NOT BAD}}
\]

Less than 3% error.

(b) Bubble point

\( \Rightarrow \) Essentially all liquid.

\( \Rightarrow \) Overall composition \( \approx \frac{K_i}{y_i} \)

<table>
<thead>
<tr>
<th>( p = 500 ) psi</th>
<th>( p = 400 ) psi</th>
<th>( p = 385 ) psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Species} )</td>
<td>( K_i )</td>
<td>( K_i x_i )</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>0.1</td>
<td>4.2</td>
</tr>
<tr>
<td>( \text{C}_2 \text{H}_6 )</td>
<td>0.2</td>
<td>0.9</td>
</tr>
<tr>
<td>( \text{C}_3 \text{H}_8 )</td>
<td>0.7</td>
<td>0.27</td>
</tr>
</tbody>
</table>

\[
\frac{0.789}{\text{decrease } P}
\]

\[
\begin{array}{c}
\frac{0.927}{\text{slightly lower } P} \\
\frac{0.964}{\text{less than 47% error}}
\end{array}
\]

Next, flash calculations.
**Flash Calculations**

SINGLE STAGE SEPARATION BASED ON VLE.

\[ \begin{align*}
F & \rightarrow \text{Vapor, } y_i \rightarrow V \\
\text{Feed, } z_i & \rightarrow \text{Liquid, } x_i \rightarrow L
\end{align*} \]

@ EQUILIBRIUM \((T, P)\)

**What do we usually know?**

\( F, z_i, T, P \)

**What are looking for?**

\( V, L, y_i, x_i \)

**Equations:**

\[ \begin{align*}
\sum_i x_i &= 1 \\
\sum_i y_i &= 1 \\
y_i &= k_i x_i \\
F &= L + V \\
F z_i &= L x_i + V y_i
\end{align*} \]
For ideal gas/ideal liquid

\[ K_i = \frac{p_i^{\text{sat}}}{p} \]  
\[ + \frac{p_i^{\text{sat}}}{p_i^{\text{sat}}} = f(L) \text{ only} \]

We can combine equations to get one variable in terms of knowns.

**Overall:**  
\[ F = L + V \Rightarrow L = F - V \]

**Component:**  
\[ z_i F = x_i L + y_i V \]

**Substitute:**

\[ y_i = \frac{1}{V} \left[ z_i F - x_i (F - V) \right] \]

\[ x_i = \frac{y_i}{K_i} \]

**Phase Equilibria:**

**Substitute,**
\[ \frac{V}{F} K_i y_i = z_i K_i - y_i \left( 1 - \frac{V}{F} \right) \]
\[ y_i \left( \frac{V}{F} K_i + 1 - \frac{V}{F} \right) = z_i K_i \]
\[ y_i \left( 1 + \frac{V}{F} (K_i - 1) \right) = z_i K_i \]
\[ y_i = \frac{z_i K_i}{\left( 1 + \frac{V}{F} (K_i - 1) \right)} \]

But \[ \sum_i y_i = 1 \]
\[ 1 = \sum_i \left( \frac{z_i K_i}{\left( 1 + \frac{V}{F} (K_i - 1) \right)} \right) \]
**Example 10.5**  The system acetone (1) / acetonitrile (2) / nitromethane (3) at 80 °C and 110 kPa has the overall composition ω_1 = 0.45, ω_2 = 0.35, and ω_3 = 0.20. Assuming that Raoult’s Law is appropriate to this system, determine L, V, x_i, and y_i. The vapor pressures of the pure species at 80 °C are:

\[ p_{1}^{\text{sat}} = 195.75 \text{ kPa} \quad p_{2}^{\text{sat}} = 97.84 \text{ kPa} \quad p_{3}^{\text{sat}} = 50.32 \text{ kPa} \]

**Solution:**

**Step 1: Bubble P**

All liquid out so \( \omega_i = x_i \)

\[
P_{\text{Bubble}} = x_1 p_{1}^{\text{sat}} + x_2 p_{2}^{\text{sat}} + x_3 p_{3}^{\text{sat}}
\]

\[
= (0.45)(195.75) + (0.35)(97.84) + (0.2)(50.32)
\]


\[ P_{\text{bubble}} = 132.4 \text{ kPa} \]

**STEP 2: DEW P**

All vapor out so \( z_i = y_i \)

\[ P_{\text{Dew}} = \frac{1}{\frac{y_1}{p_1} + \frac{y_2}{p_2} + \frac{y_3}{p_3}} \]

\[ = \frac{1}{\frac{0.45}{195.75} + \frac{0.35}{97.84} + \frac{0.2}{50.32}} \]

\[ P_{\text{Dew}} = 101.5 \text{ kPa} \]

**Why calculate \( P_{\text{bubble}} \) and \( P_{\text{Dew}} \)?**

Set upper and lower bounds on \( P \).

(Only holds for ideal gas \& ideal liquid)
\[ P = 110 \text{ kPa} \Rightarrow \text{2 PHASE} \Rightarrow \text{FLASH} \]

\[ K_i = \frac{P_i}{P} \quad \text{(RAOUlt's Law)} \]

\[ K_1 = \frac{195.75}{110} = 1.7775 \]

\[ K_2 = \frac{97.84}{110} = 0.8895 \]

\[ K_3 = \frac{50.32}{110} = 0.4575 \]

Choose basis: \( F = 1 \text{ mol} \)

Now, substitute into FLASH equation:

\[ I = \frac{(0.45)(1.7775)}{1 + \frac{V}{I}(1.7775-1)} + \frac{(0.35)(0.8895)}{1 + \frac{V}{I}(0.8895-1)} \]

\[ + \frac{(10.20)(0.4575)}{1 + \frac{V}{I}(0.4575-1)} \]

Solve: \( V = 0.7367 \text{ mol} \)
\[ L = F - V = 1 - 0.7367 \]

\[ L = 0.2633 \text{ mL} \]

\[ y_1 = \frac{(0.45)(1.7795)}{1 + 0.7367(1.7795 - 1)} \Rightarrow y_1 = 0.5087 \]

\[ y_2 = \frac{(0.35)(0.8895)}{1 + 0.7367(0.8895 - 1)} \Rightarrow y_2 = 0.3387 \]

\[ y_3 = \frac{(0.20)(0.4575)}{1 + 0.7367(0.4575 - 1)} \Rightarrow y_3 = 0.1524 \]

**Double Check:** \( \sum y_i = 1 \)

**From \( K_i \), Calculate \( x_i \)**

\[ x_1 = 0.2859 \]

\[ x_2 = 0.3810 \]

\[ x_3 = 0.333 \]

**Double Check:** \( \sum x_i = 1 \)