Chemical Engineering Thermodynamics

Vapor/Liquid Equilibrium: Introduction and Application

Mohammad Fadil Abdul Wahab
Consider a multicomponent system in a VLE condition, the fugacity (to be defined in Chapter 11) of species $i$ for each phase is given by,

For vapor mixture
\[ \hat{f}_i^v = \hat{\phi}_i y_i P \]

For liquid solution
\[ \hat{f}_i^l = \gamma_i x_i f_i \]

VLE criteria (to be shown/derived in chapter 11),
\[ \hat{f}_i^l = \hat{f}_i^v \]

so
\[ \hat{\phi}_i y_i P = \gamma_i x_i f_i \]

where,
- $\hat{\phi}_i$ fugacity coefficient of species $i$ in gas mixture
- $f_i$ fugacity of pure species $i$
- $\gamma_i$ activity coefficient of species $i$ in liquid solution
Raoult's Law

For ideal gas vapor mixture in equilibrium with ideal liquid solution

\[ \gamma_i = 1 \]

\[ \hat{\phi}_i = 1 \]

equation becomes

\[ y_i P = x_i f_i \]

and also for pure species in equilibrium and ideal gas vapor,

\[ f_i = f_i^l = f_i^v = P = P_i^{sat} \]

we get,

\[ y_i P = x_i P_i^{sat} \quad \text{Raoult's Law} \quad (10.1) \]
Modified Raoult’s Law

\[ \hat{\phi}_i = 1 \]

For ideal-gas mixture in equilibrium with non-ideal liquid solution

\[ \hat{\phi}_i y_i P = \gamma_i x_i f_i \]

\[ y_i P = \gamma_i x_i P_i^{\text{sat}} \quad \text{Modified Raoult's Law} \quad (10.5) \]

where \( \gamma_i \) is a function of \( T \) and \( x_i \).
K-value \((K_i)\)

\[
K_i = \frac{y_i}{x_i} \quad (10.10)
\]

If Raoult’s Law is valid,

\[
y_i P = x_i P_{i}^{sat}
\]

\[
K_i = \frac{P_{i}^{sat}}{P} \quad (10.11)
\]

If Modified Raoult’s Law is valid,

\[
y_i P = x_i \gamma_i P_{i}^{sat}
\]

\[
K_i = \frac{\gamma_i P_{i}^{sat}}{P} \quad (10.12)
\]
K-value Using DePriester Chart

For light hydrocarbon mixture (commonly found in industry),

$K_i$ is essentially function of $T$ and $P$ only.

$K_i$ are tabulated in a chart called the DePriester chart.
Bubblepoint & Dewpoint Calculations
To calculate the $P$ when the 1st bubble appear as a result of decrease in $P$ at constant $T$. Also calculate the bubble’s composition $\{y_i\}$.

or

To calculate the $P$ when the last bubble disappear as a result of increase in $P$ at constant $T$. Also calculate the composition $\{y_i\}$ of this bubble.
DEW P: Calculate \( \{x_i\} \) and P, given \( \{y_i\} \) and T

To calculate the P when the 1st dew (a drop of liquid) appear as a result of increase in P at constant T. Also calculate the composition \( \{x_i\} \) of this dew.

or

To calculate the P when the last dew disappear as a result of decrease in P at constant T. Also calculate the composition \( \{x_i\} \) of this dew.
BUBL T: Calculate \( \{y_i\} \) and \( T \), given \( \{x_i\} \) and \( P \)

To calculate the \( T \) when the 1st bubble appear as a result of increase in \( T \) at constant \( P \). Also calculate the composition \( \{y_i\} \) of this bubble.

or

To calculate the \( T \) when the last bubble disappear as a result of decrease in \( T \) at constant \( P \). Also calculate the composition \( \{y_i\} \) of this bubble.
DEW T: Calculate \( \{x_i\} \) and \( T \), given \( \{y_i\} \) and \( P \)

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or

To calculate the \( T \) when the last dew disappear as a result of increase in \( T \) at constant \( P \). Also calculate the composition \( \{x_i\} \) of this dew.
Derivation

Overall mole balance

\[ T = L + V \]

Component mole balance,

\[ Tz_i = Lx_i +Vy_i \]

Let \( T = 1 \) mol, so \( V \) and \( L \) are mole fractions,

\[ z_i = Lx_i + Vy_i \]

\[ z_i = (1 - V)x_i + Vy_i \quad (A) \]

Note: \( z_i \) is overall composition.
Substitute \( y_i = K_i x_i \) into (A),

\[
z_i = (1 - V)x_i + K_i x_i V = x_i (1 - V + VK_i) = x_i (1 + V (K_i - 1))
\]

\[
x_i = \frac{z_i}{1 + V (K_i - 1)}
\]

Substitute \( x_i = \frac{y_i}{K_i} \) into (A),

\[
z_i = (1 - V) \frac{y_i}{K_i} + y_i V \\
z_i K_i = (1 - V) y_i + y_i VK_i
\]

\[
y_i = \frac{z_i K_i}{1 + V (K_i - 1)} \quad \text{(10.16)}
\]
Also,

\[ \sum x_i - \sum y_i = 0 \]

\[ \sum \frac{z_i}{1+V(K_i-1)} - \sum \frac{z_i K_i}{1+V(K_i-1)} = 0 \]

\[ \sum \frac{z_i - z_i K_i}{1+V(K_i-1)} = 0 \]
Bubblepoint Calculation

At bubble point (practically all liquid) L=1, V=0 and \( z_i = x_i \)

\[
\sum \frac{z_i - z_i K_i}{1 + V(K_i - 1)} = 0 \text{ becomes,}
\]

\[
\sum (x_i - x_i K_i) = 0
\]

\[
\sum x_i = \sum x_i K_i
\]

\[
\sum x_i K_i = 1 \quad (10.13) \quad \text{Bubblepoint criteria}
\]
If Raoult's Law valid,

\[ \sum x_i K_i = \sum x_i \frac{P_i^{sat}}{P} = 1 \quad \text{so,} \quad P = \sum x_i P_i^{sat} \quad (10.2) \]

see example 10.1

If Modified Raoult's Law valid,

\[ \sum x_i K_i = \sum x_i \frac{\gamma_i P_i^{sat}}{P} = 1 \quad \text{so,} \quad P = \sum x_i \gamma_i P_i^{sat} \quad (10.6) \]

see example 10.3
Dewpoint Calculation

At dewpoint (practically all vapor): \( L=0, \ V=1 \) and \( z_i = y_i \)

\[
\sum \frac{z_i - z_i K_i}{1 + V(K_i - 1)} = 0
\]

becomes,

\[
\sum \frac{y_i - y_i K_i}{K_i} = 0
\]

\[
\sum \frac{y_i}{K_i} - \sum y_i = 0
\]

\[
\sum \frac{y_i}{K_i} = 1 \quad (10.14)
\]

Dewpoint criteria
If Raoult's Law valid,

\[ \sum \frac{y_i}{K_i} = \sum \frac{y_i}{P_i^{sat}} = 1 \quad P = \frac{1}{\sum \frac{y_i}{P_i^{sat}}} \quad (10.3) , \]

see example 10.1

If Modified Raoult's Law valid,

\[ \sum \frac{y_i}{K_i} = \sum \frac{y_i}{\gamma_i P_i^{sat}} = 1 \quad P = \frac{1}{\sum \frac{y_i}{\gamma_i P_i^{sat}}} \quad (10.7) , \]

see example 10.3
Relative Volatility

$$\alpha_{ik} = \frac{y_i}{x_i} = \frac{K_i}{K_k}$$

at azeotrope $$\alpha_{ik} = \frac{1}{1} = 1$$

$$\alpha_{ik} > 1 \quad \text{Species i is relatively more volatile}$$

$$\alpha_{ik} < 1 \quad \text{Species k is relatively more volatile}$$

If Raoult's Law valid,

$$\alpha_{12} = \frac{P_{1}^{sat}}{P} = \frac{P_{1}^{sat}}{P_{2}^{sat}}$$

Note: for higher vapor pressure means more volatile $$\alpha_{12} > 1$$

If Modified Raoult's Law valid,

$$\alpha_{12} = \frac{\gamma_1 P_{1}^{sat}}{\gamma_2 P_{2}^{sat}} = \frac{\gamma_1 P_{1}^{sat}}{\gamma_2 P_{2}^{sat}}$$
Example 10.1
Plot $P_x y_1$ at $T=75^\circ C$

Mixture: Acetonitrile(1)/Nitromethane(2)

Antoine Eqn,

$$\ln P_1^{\text{sat}} / \text{kPa} = 14.2724 - \frac{2945.47}{T / ^\circ C + 224.00}$$

$$\ln P_2^{\text{sat}} / \text{kPa} = 14.2043 - \frac{2972.64}{T / ^\circ C + 209.00}$$

calculate at $75^\circ C$,

$P_1^{\text{sat}} = 83.21 \text{kPa}$ \hspace{1cm} $P_2^{\text{sat}} = 41.98 \text{kPa}$

Note: Acetonitrile(1) is more volatile.
Calculate $P$ and $y_1$, given a set of $x_1$ and $T=75^\circ$C. This is BUBL $P$ calculation.

\[
\sum x_i K_i = 1 \quad (10.13) .
\]

Let us assume Raoult's Law is valid, $P = P_b = \sum x_i P_i^{sat} \quad (10.2)$

\[
P = x_1 P_1^{sat} + x_2 P_2^{sat} = x_1 P_1^{sat} + (1-x_1) P_2^{sat}
\]

\[
P = (P_1^{sat} - P_2^{sat})x_1 + P_2^{sat} \quad \text{Eqn A} \quad \text{note: a linear line (y=mx+c)}
\]

Also, $y_1 = \frac{x_1 P_1^{sat}}{P}$ \quad \text{Eqn B}

So, Calculate $P$ for a set of $x_1$ (Eqn A) and then calculate $y_1$ (Eqn B)
So now plot \( P_{x_1} \) and \( P_{y_1} \) on Pxy diagram!!
Ex: Calculate $P_d$ and $x_1$, given $y_1=0.6$ and $T=75^\circ C$
(i.e. what is the dew P for gas mixture at 75$^\circ$C and 60% acetonitrile)

This is point c in previous $P_{x_1y_1}$ diagram.

Dew $P$ calculation (Note: $z_1=y_1$).

$$\sum \frac{y_i}{K_i} = 1 \quad (10.14), \quad \text{If Raoult's Law valid,} \quad P_d = \frac{1}{\sum \frac{y_i}{P_{sat_i}}} \quad (10.3)$$

$$P_d = \frac{1}{\frac{0.6}{83.21} + \frac{0.4}{41.98}} = 59.74kPa$$

Compare with values from $P_{xy}$ diagram.

Then calculate $x_1$ using,

$$x_1 = \frac{y_1P_d}{P_{sat_1}} = \frac{0.6(59.74)}{83.21} = 0.43$$
• We could also plot Pxy diagram using DEW pressure calculation.

• Set $y_i$, calculate $P_d$ and $x_i$.

• Plot Pxy using $P_d x_i y_i$

• DIY.....
Plot $T_x y_1$ at $P=70\text{kPa}$

Mixture: Acetonitrile(1)/Nitromethane(2)

Antoine Eqn,

$$T_{1{\text{sat}}}^{\circ C} = \frac{2945.47}{14.2724 - \ln P/\text{kPa}} - 224.00$$

$$T_{2{\text{sat}}}^{\circ C} = \frac{2972.64}{14.2043 - \ln P/\text{kPa}} - 209.00$$

so at 70kPa,

$$T_{1{\text{sat}}} = 69.84^{\circ C} \quad T_{2{\text{sat}}} = 89.58^{\circ C}$$

As expected Acetonitrile(1) is more volatile
\[ \sum x_i K_i = 1 \quad (10.13) \]

For Raoult's Law, \( P = P_b = \sum x_i P_{i}^{sat} \quad (10.2) \)

\[
P = x_1 P_{1}^{sat} + x_2 P_{2}^{sat} = x_1 P_{1}^{sat} + (1 - x_1) P_{2}^{sat}
\]

\[
x_1 = \frac{P - P_{2}^{sat}}{P_{1}^{sat} - P_{2}^{sat}} \quad \text{Eqn C}
\]

Note: Since we used BUBL point calculation, \( T = T_b \)

Choose \( T \) between \( T_{1}^{sat} \) and \( T_{2}^{sat} \), then using Antoine eqns calculate \( P_{1}^{sat} \) and \( P_{2}^{sat} \) at the chosen \( T \) and then calculate \( x_1 \) by Eqn C.

Then calculate \( y_1 \) using,

\[
y_1 = \frac{x_1 P_{1}^{sat}}{P}
\]
Plot $T_{x_1}y_1$ at $P=70$ kPa

Given or Set

$$x_1 = \frac{P - P_2^{sat}}{P_1^{sat} - P_2^{sat}}$$

$$y_1 = \frac{x_1 P_1^{sat}}{P}$$

<table>
<thead>
<tr>
<th>P (kPa)</th>
<th>$T=T_b^{(oC)}$</th>
<th>$T_1^{sat}$</th>
<th>$x_1$ $T_2^{sat}$</th>
<th>$y_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>69.84 $T_1^{sat}$</td>
<td>1 $(x_2=0)$</td>
<td>1 $(y_2=0)$</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>74</td>
<td>0.7378</td>
<td>0.8484</td>
<td></td>
</tr>
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<td>70</td>
<td>78</td>
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<td>0.6759</td>
<td></td>
</tr>
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<td>70</td>
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<td>0.4742</td>
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</tr>
<tr>
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<td>86</td>
<td>0.1424</td>
<td>0.2401</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>89.58 $T_2^{sat}$</td>
<td>0 $(x_2=1)$</td>
<td>0 $(y_2=1)$</td>
<td></td>
</tr>
</tbody>
</table>

So now plot $T_{x_1}$ and $T_{y_1}$ on a Txy diagram!!
Ex: Calculate $T_b$ and $y_1$, given $x_1=0.6$ and $P=70\text{kPa}$.
(i.e. calculate the bubble temperature at 70kPa and 60% acetonitrile)

This is point b in previous $T_{x_1y_1}$ diagram. Note: $z_1=x_1$

Bubble temperature calculation!!

\[ \sum x_i K_i = 1 \quad (10.13), \]

The solution is not straightforward as $T$ is unknown. Let’s see how to solve mathematically,

For Raoult's Law, $P_b = \sum x_i P_{i}^{sat} \quad (10.2)$

\[ P_b = \frac{P_k^{sat}}{P_k^{sat}} \sum x_k P_k^{sat} = P_k^{sat} \sum x_i \frac{P_i^{sat}}{P_k^{sat}} = P_k^{sat} \sum x_i \alpha_{ik} \]

where $k$ is a component that arbitrarily chosen.
\[ P_b = P_k^{\text{sat}} \sum x_i \alpha_{ik} \]

where \( \alpha_{ik} = \frac{P_i^{\text{sat}}}{P_k^{\text{sat}}} \) is relative volatility of \( i \) wrt \( k \).

\[ P_k^{\text{sat}} = \frac{P_b}{\sum x_i \alpha_{ik}} \quad \text{(A)} \]

Also,

\[ \ln \alpha_{ik} = \ln \frac{P_i^{\text{sat}}}{P_k^{\text{sat}}} = \ln P_i^{\text{sat}} - \ln P_k^{\text{sat}} = \left( A_i - \frac{B_i}{T + C_i} \right) - \left( A_k + \frac{B_k}{T + C_k} \right) \]
Solution is through iteration,

1. Start with an initial guess of $T$ as follows,

$$T = \sum x_i T_{i}^{sat}$$

$$T = 0.6(69.84) + 0.4(89.58) = 77.74^\circ C$$

2. Arbitrarily pick a component, e.g. Nitromethane so, $k=2$

3. Calculate $\alpha_{ik}$,

   (note: Number of $\alpha_{ik}$ is equal to total number of component)

$$\ln \alpha_{ik} = \left( A_i - \frac{B_i}{T + C_i} \right) - \left( A_k + \frac{B_k}{T + C_k} \right)$$

we get,

$$\alpha_{12} = 1.9611$$

$$\alpha_{22} = 1$$
4. Calculate $P_{k}^{\text{sat}}$ using eqn A,

$$P_{k}^{\text{sat}} = \frac{P}{\sum x_{i} \alpha_{ik}}$$

$$P_{2}^{\text{sat}} = \frac{P}{x_{1} \alpha_{12} + x_{2} \alpha_{22}} = \frac{70}{0.6(1.9611)+0.4(1)} = 44.3977\text{kPa}$$

5. Calculate a new value of $T$ using the Antoine eqn,

$$T = \frac{B_{k}}{A_{k} - \ln P_{k}^{\text{sat}}} - C_{k}$$

$$T = \frac{2972.64}{14.2043 - \ln 44.3977} - 209 = 76.53^\circ C$$

6. Stop if this $T$ is equal or close to earlier value of $T$, else use this value as a new guess. Repeat steps 3, 4 & 5 until converge.
7. Finally, calculate $y_i$ using Raoult’s law (Use the Antoine Eqn for $P_i^{sat}$)

$$y_1 = 0.7472$$

<table>
<thead>
<tr>
<th>$T$</th>
<th>$a_{12}$</th>
<th>$P_2^{sat}$</th>
<th>$T$</th>
</tr>
</thead>
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<td>77.74</td>
<td>1.9611</td>
<td>44.39</td>
<td>76.53</td>
</tr>
<tr>
<td>76.53</td>
<td>1.9703</td>
<td>44.24</td>
<td>76.43</td>
</tr>
<tr>
<td>76.43</td>
<td>1.9717</td>
<td>44.22</td>
<td>76.42</td>
</tr>
</tbody>
</table>
DEW T calculation

Calculate $T_d$ and $x_1$, given $y_1$ and $P$.

Example: Calculate $T_d$ and $x_1$ for $z_1 = y_1 = 0.6$ and $P = 70\text{kPa}$. See page 356 for the solution (also by iteration) of DEW T calculation.

Answer: $T_d = 79.58^\circ\text{C}$
$x_1 = 0.4351$
Example 10.4

Calculation of dew pressure and bubble pressure using K-value from DePriester chart.

Note: Why the solution is by trial and error?
Flash Calculation
Flash Calculation

An important application of VLE!

Liquid at pressure equal or higher than $P_b$ “flashes” or partially evaporates when the $P$ is reduced, thus producing a vapor and liquid.

Flash calculation is to determine $V$, $L$, $\{x_i\}$, and $\{y_i\}$ at $T$ and $P$ by assuming VLE.

Note: $\{x_i\}$ composition of liquid and $\{y_i\}$ composition of vapor
As derived for VLE system,

\[ y_i = \frac{z_i K_i}{1 + V(K_i - 1)} \quad (10.16) \]

\[ \sum y_i = 1, \quad \text{so:} \]

\[ \sum \frac{z_i K_i}{1 + V(K_i - 1)} = 1 \quad (10.17) \]

Solution is by trial and error.

Guess \( V \) until the summation term equal to 1.

But………. 

.........first we need to know whether the system is actually two-phase. In general ......

If $P_d < P < P_b$, two phase

or

If $T_b < T < T_d$, two phase
Examples of Flash Calculation

Example 10.5:
Flash calculation for system where Raoult’s Law valid

Example 10.6:
Flash calculation using K-value from DePriester Chart
Dewpoint T of Mixture of Water Vapor and Non-condensable Gases

This is a special case of dew T calculation.
Solution is straightforward by the application of Raoult’s Law to the condensable component H_2O (here identified as component 2).

The system contains a dew (liquid water) in VLE with mixture of water vapor and non-condensable gases (such as N_2, CO_2, O_2 etc.).

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

The dew is 100% H_2O, so \( x_2 = 1 \)

so \( P_2^{sat} = y_2 P \)
Example

Dewpoint T of Combustion Products

For stoichiometric combustion of methane, calculate dew point $T$ of the combustion products.

$$\text{CH}_4 + 2\text{O}_2 + 2(79/21)\text{N}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 2(79/21)\text{N}_2$$

Mole fraction of $\text{H}_2\text{O}$ is $\frac{2}{1+2+2(79/21)} = 0.19$

$$P_2^{\text{sat}} = y_2 P \quad P_2^{\text{sat}} = 0.19(101.325\text{kPa}) = 19.25\text{kPa}$$

From steam table*, $T_d = T_2^{\text{sat}} = 59.5^\circ\text{C}$

*You could also use Antoine Eqn.
Henry’s Law
Henry’s Law is VLE relation that is valid for ideal-gas mixture in equilibrium with a dilute solution, where we want to know the composition of dissolve gas $i$ in the dilute solution.

For example,

a) CO$_2$ and H$_2$O system.

b) Air and H$_2$O system.

\[
\hat{\phi}_i y_i P = \gamma_i x_i f_i \\
y_i P = x_i \gamma_i f_i = x_i \gamma_i P^{sat} \\
\text{let } H_i = \gamma_i f_i = \gamma_i P^{sat}
\]

$H_i$ is Henry’s constant (in bar) for dissolved gas ($i$).

so \[y_i P = x_i H_i \quad \text{Henry’s Law}\]
$y_iP = x_iH_i$

So at dilute solution,
$y_i = \left(\frac{H_i}{P}\right) x_i$

For constant system pressure $P$,
$y_i = (\text{Constant})x_i$

If we plot $y_i$ vs $x_i$, we get a straight line through the origin.

So Henry’s constant for dissolved gas ($i$) can be easily determined from experiment.
In previous example of dewpoint for combustion product, we assume the liquid is all \( \text{H}_2\text{O} \) \( (x_2=1) \).

What if we want to know the mole fraction of dissolved \( \text{CO}_2 \) (component 1) in the dew (liquid)?

We could solve this using Henry’s Law for dissolved gases \( \text{CO}_2 \).
Apply Henry’s law for component 1.

Use $H_1$ data from Table 10.1 (note: this actually valid at 25°C).

\[
x_1 = \frac{y_1 P}{H_1} = \frac{(1/(1+2+7.52))(1.013\text{bar})}{1670\text{bar}} = 3.4622 \times 10^{-5} \approx 0
\]

As expected, only small amount of CO$_2$ present in liquid water.

See also example 10.2
If the fugacity of \( i \) in liquid phase is given by Henry’s Law,

\[
\hat{f}_i = \gamma_i x_i f_i = x_i H_i
\]

If the gas is ideal solution (Lewis/Randall is valid),

\[
\hat{f}_i^{id} = \phi_i y_i P
\]

So we get the following version of Henry’s Law if gas mixture is ideal solution,

\[
\phi_i y_i P = x_i H_i
\]
Extension of Example 10.3

Plot $P_x_1 y_1$ and $x_1 y_1$ diagrams at $T=318.15K$

From bubblepoint calculation,

Set $x_1$
Calculate $P_b$
Calculate $y_1$
<table>
<thead>
<tr>
<th>x1</th>
<th>G1</th>
<th>G2</th>
<th>P</th>
<th>y1</th>
</tr>
</thead>
<tbody>
<tr>
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<td>3.03</td>
<td>1.00</td>
<td>65.64</td>
<td>0.00</td>
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<td>72.97</td>
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<td>1.72</td>
<td>1.10</td>
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<td>0.35</td>
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<td>1.15</td>
<td>73.73</td>
<td>0.34</td>
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<td>0.40</td>
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<td>1.00</td>
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</table>

G1 is gamma1
Locate azeotropic pressure at \( T=318.15 \text{K} \) and its composition.
Locate BUBL P at T=318.15K, \( x_1 = 0.25 \)
Locate DEW P at $T=318.15\,K$, $y_1=0.6$.
Locate azeotropic composition at 318.15K

\[ T = 318.15 \]

\[ \alpha_{12} > 1 \]
A stream of mixture of methanol(1)/methyl acetate(2) is inside a pipeline where the T is 318.15K and P is 66kPa. The stream contains (60 mole percent methanol). What is the phase of the stream?
Let’s check bubble pressure and dew pressure.

From example 10.3b), Dew P is 62.89kPa

Now calculate bubble P,

\[ P_b = x_1 \gamma_1 P_{1}^{sat} + x_2 \gamma_2 P_{2}^{sat} = 71kPa \]

\( P_d < P < P_b \) hence two phases!

Locate the conditions on the following \( Px_1y_1 \) diagram.

Determine \( V, L, \{x_i\} \) and \( \{y_i\} \) using flash calculation.
T=318.15

Series1
Series2
\[ K_1 = \frac{P_{1}^{sat} \gamma_1}{P} = \frac{P_{1}^{sat} \exp(A(x_2)^2)}{P} \]
\[ K_2 = \frac{P_{2}^{sat} \exp(A(x_1)^2)}{P} \]

We need \( x_1 \) !! Let's us do bubble point calculation at
\( P = 66 \text{kPa}, T = 318.15 \text{K} \) and \( x_1 \)

\[ P_b = 66 \text{kPa} = x_1 \gamma_1 P_{1}^{sat} + x_2 \gamma_2 P_{2}^{sat} \quad \text{(a)} \]
\[ K_1 = \frac{P_1^{sat} \gamma_1}{P} = \frac{P_1^{sat} \exp(A(x_2)^2)}{P} \]
\[ K_2 = \frac{P_2^{sat} \exp(A(x_1)^2)}{P} \]
so (a) becomes,

\[ 66 = x_1 P_1^{sat} \exp(A(1 - x_1)^2) + (1-x_1) P_2^{sat} \exp(A(x_1)^2) \]
66 = x_1(44.51)\exp(1.107)(1 - x_1)^2) + (1-x_1)(65.64)\exp(1.107(x_1)^2)

Guess x_1,

\begin{align*}
x_1 &= 0.7 \quad P=68.29 \\
x_1 &= 0.8 \quad P=63.88 \\
x_1 &= 0.75 \quad P=66.36 \\
x_1 &= 0.76 \quad P=65.91 \ldots \text{good enough}
\end{align*}
Now we can calculate $K_1$ and $K_2$ for flash calculation,

$$K_1 = \frac{P_1^{sat} \gamma_1}{P} = \frac{44.51 \exp(1.107(1 - 0.76)^2)}{66} = 0.719$$

$$K_2 = \frac{65.64 \exp(1.107(0.76)^2)}{66} = 1.885$$
Substitute into eqn (10.17),

\[ \sum \frac{z_i(K_i)}{1 + V(K_i - 1)} = 1 \]

\[ \frac{0.6(0.719)}{1 + V(0.719 - 1)} + \frac{(1 - 0.6)(1.885)}{1 + V(1.885 - 1)} = 1 \]  
(10.17)

\[ \frac{0.431}{1 - 0.281V} + \frac{0.754}{1 + 0.885V} = 1 \]
\[
\frac{0.431}{1 - 0.281V} + \frac{0.754}{1 + 0.885V} = 1
\]

Guess, \( \sum = 1 \)

\begin{align*}
V=0.50 & \quad 1.024 \\
V=0.55 & \quad 1.017 \\
V=0.70 & \quad 1.002 \\
V=0.75 & \quad 0.999 \\
V=0.73 & \quad 1.000
\end{align*}

So \( V=0.73 \) \quad \text{L}=1-V=0.27
\[ y_i = \frac{z_i K_i}{1 + V(K_i - 1)} \]  

(10.16)

\[ y_1 = \ldots \]

\[ y_2 = \ldots \]

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

\[ x_1 = \ldots \]

\[ x_2 = \ldots \]