Thermodynamics II

Lec 3: Vapor Liquid Equilibrium-part 3

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Content

- **K-value**
- **Relative volatility**
- **Bubble and dew point calculations**
- **Flash separation**
K-value

$$K_i \equiv \frac{y_i}{x_i}$$

is the equilibrium ratio

- A measure of the tendency of a given chemical species to partition itself preferentially between liquid and vapor phases
- It does serve as a measure of the "lightness" of a constituent species,

If Raoult's Law is valid,

$$y_i P = x_i P_i^{sat}$$

$$K_i = \frac{P_i^{sat}}{P}$$

Independent of the V or L composition

If Modified Raoult's Law is valid,

$$y_i P = x_i \gamma_i P_i^{sat}$$

$$K_i = \frac{\gamma_i P_i^{sat}}{P}$$

Specify two of (P, T, volatility)

Consider a pure compound:
- for a given P, find T_{bp} (i.e., K = 1)
- for a given T, find P_{sat} (i.e., K = 1)
- for a given P, T, find K
  - K > 1 prefers vapor phase
  - K < 1 prefers liquid phase

DePriester Chart

Don't extrapolate beyond the range of the chart.
Figure 2-11 Modified DePriester chart (in S.I. units) at low temperatures

At 2000 kPa, what is the boiling point of ethane?

At 15 °C, what is the saturated vapor pressure of isobutane?

At 0 °C and 500 kPa, what is the volatility of n-hexane?

- for a given P, find \( T_{bp} \) (i.e., \( K = 1 \))
- for a given T, find \( P_{sat} \) (i.e., \( K = 1 \))
- for a given P, T, find K
  - \( K > 1 \) prefers vapor phase
  - \( K < 1 \) prefers liquid phase

From Separation Process Engineering, Third Edition by Phillip C. Wankat
(ISBN: 0131382276) Copyright © 2012 Pearson Education, Inc. All rights reserved.
Example

- Use the DePriester chart to generate the temperature-composition diagram for isobutane and propane at 1000 kPa.

Example Cont.

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Dew point and Bubble point Calculations

➢ For VLE system,

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,

\[ z_i = Lx_i + Vy_i \]
\[ z_i = (1 - V)x_i + Vy_i \]  \( \text{(A)} \)

Note: \( z_i \) is overall composition.

Substitute \( y_i = K_i x_i \) into (A),

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

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

Volatility: \[ K_i = \frac{y_i}{x_i} \]  \( \text{(10.10)} \)

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

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

\[ y_i = \frac{z_i K_i}{1 + V(K_i - 1)} \]
Dew point and Bubble point Calculations

Also,

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

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

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

Bubble point Calculations

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

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

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

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

\[ \Rightarrow \sum x_i K_i = 1 \quad \text{Bubblepoint criteria} \]
Bubble point Calculations

If Raoult's Law valid, \[ y_i P = x_i P_{i}^{sat} \quad \Rightarrow \quad K_i = \frac{P_{i}^{sat}}{P} \]

\[ \sum x_i K_i = \sum x_i \frac{P_{i}^{sat}}{P} = 1 \quad \text{so,} \quad P = \sum x_i P_{i}^{sat} \]

see example 10.1

If Modified Raoult's Law valid, \[ y_i P = x_i \gamma_i P_{i}^{sat} \quad \Rightarrow \quad K_i = \frac{\gamma_i P_{i}^{sat}}{P} \]

\[ \sum x_i K_i = \sum x_i \frac{\gamma_i P_{i}^{sat}}{P} = 1 \quad \text{so,} \quad P = \sum x_i \gamma_i P_{i}^{sat} \]

Dew point Calculations

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

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

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

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

\[ \Rightarrow \quad \sum \frac{y_i}{K_i} = 1 \quad \text{Dewpoint criteria} \]
Dew point Calculations

If Raoult's Law valid,

$$\sum \frac{y_i}{K_i} = \sum \frac{y_i}{P_i^{sat}} = 1 \quad P = \frac{1}{\sum \frac{y_i}{P_i^{sat}}}$$

If Modified Raoult's Law valid,

$$\sum \frac{y_i}{K_i} = \sum \frac{y_i}{\gamma_i P_i^{sat}} = 1 \quad P = \frac{1}{\sum \frac{y_i}{\gamma_i P_i^{sat}}}$$

Example

Flash Calculation - Raoult's Law

A liquid that is 40% component 1 and 60% component 2 is flashed to 1200 kPa. The outlet temperature is 150°C.

$$P_{1}^{sat} = 15 - 3000/(T+250) \quad T \text{°C}$$
$$P_{2}^{sat} = 14 - 2900/(T+200)$$

Calculate the fraction that is liquid and the composition of the liquid and vapor phases.
Example Cont.
Example Cont.

\[
\begin{array}{c|c|c}
\text{P} & 1200 & \text{L/F} 0.7036 \\
\hline
\text{T} & 150 & \\
\hline
z_1 & 0.4 & \text{x}_1 = \frac{z_1r}{(K_1r + L_1rF^*(1-K_1r))} \\
\hline
z_2 & 0.6 & \text{x}_2 = \frac{z_2r}{(K_2r + L_2rF^*(1-K_2r))} \\
\hline
P_{1sat} & = \text{EXP}(15-3000/(T+250)) & \text{y}_1 = K_1r\cdot x_1 \\
\hline
P_{2sat} & = \text{EXP}(14-2700/(T+200)) & \text{y}_2 = K_2r\cdot x_2 \\
\hline
K_1 & = \frac{P_{1sat}}{P} & \text{x}_1 + \text{x}_2 = \text{x}_1r + \text{x}_2r \\
\hline
K_2 & = \frac{P_{2sat}}{P} & \text{y}_1 + \text{y}_2 = \text{y}_1r + \text{y}_2r \\
\end{array}
\]

\[\text{Sum}_i \cdot \text{Sum}_j = \text{F10-F11}\]
General VLE equilibrium criteria

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  \[ f_i^v = \hat{\phi}_i y_i P \]

For liquid solution  \[ f_i^l = \gamma_i x_i f_i \]

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  species $i$ in gas mixture

$f_i$  fugacity of pure species $i$

$\gamma_i$  activity coefficient of species $i$ in liquid solution

General equilibrium criteria

For ideal gas vapor mixture in equilibrium with ideal liquid solution

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,  \[ y_i P = x_i P_i^{sat} \]   Raoult's Law  \[ (10.1) \]
General VLE equilibrium criteria

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

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

\[ y_i P = \gamma_i x_i P_{i}^{\text{sat}} \quad \text{Modified Raoult's Law} \]

where \( \gamma_i \) is a function of T and \( x_i \).

Using data from vapor pressure tables

Raoult’s Law

ideal liquid: \( P_A = x_A P_{A}^{\text{sat}}(T) \)

non-ideal liquid: \( P_A = \gamma_A x_A P_{A}^{\text{sat}}(T) \)

Dalton’s Law

ideal gas: \( y_A = \frac{P_A}{P_{\text{TOTAL}}} \)

non-ideal gas: \( y_A = \frac{P_A}{\phi_A P_{\text{TOTAL}}} \)

\( \phi \) : fugacity coefficient

\( \gamma \) : activity coefficient

\( P_{i}^{\text{sat}} \) : vapor pressure

Using data from vapor pressure tables
Relative volatility

Volatility

\[ K_A = \frac{y_A}{x_A} = K_A(T) \]

Strong function of temperature

Relative volatility of A wrt B

\[ \alpha_{AB} = \frac{K_A}{K_B} = \frac{y_A}{x_A} \frac{x_B}{y_B} \]

Not a strong function of temperature; often assumed independent

For a binary system, substitute and rearrange:

\[ y_B = 1 - y_A \]
\[ x_B = 1 - x_A \]

\[ y_A = \frac{\alpha_{AB} x_A}{1 + (\alpha_{AB} - 1)x_A} \]

Relative volatility

At azeotrope \( \alpha_{ik} = \frac{1}{1} = 1 \)

\( \alpha_{ik} > 1 \) Species i is relatively more volatile

\( \alpha_{ik} < 1 \) Species k is relatively more volatile

If Raoult's Law valid,

\[ \alpha_{12} = \frac{P_{1\text{sat}}}{P_{2\text{sat}}} \]
\[ \frac{P_1}{P_2} = \frac{P_{1\text{sat}}}{P_{2\text{sat}}} \leftarrow \text{Note: for higher vapor pressure means more volatile } \alpha_{12} > 1 \]

If Modified Raoult's Law valid,

\[ \alpha_{12} = \frac{\gamma_1 P_{1\text{sat}}}{\gamma_2 P_{2\text{sat}}} \]
\[ \frac{\gamma_1 P_1}{\gamma_2 P_2} = \frac{\gamma_1 P_{1\text{sat}}}{\gamma_2 P_{2\text{sat}}} \]
Relative volatility

For Raoult's Law, \( P_b = \sum x_i P_{i}^{\text{sat}} \)  \hspace{1cm} (10.2)

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

where \( k \) is a component that arbitrarily chosen.

\[
P_b = P_k^{\text{sat}} \sum x_i \alpha_{ik}
\]

Also,

\[
\ln \alpha_{ik} = \ln \frac{P_{i}^{\text{sat}}}{P_k^{\text{sat}}} = \ln P_{i}^{\text{sat}} - \ln P_k^{\text{sat}} = \left( A_i - \frac{B_i}{T + C_i} \right) - \left( A_k + \frac{B_k}{T + C_k} \right)
\]

Example

Ex: Calculate \( T_b \) and \( y_1 \), given \( x_1 = 0.6 \) and \( P = 70 \text{kPa} \).

Acetonitrile (1) / nitromethane (2)

\[
\ln \frac{P_2^{\text{sat}}}{kPa} = 14.2043 - \frac{2972.64}{t / ^\circ C + 209.00}
\]

\[
\ln \frac{P_1^{\text{sat}}}{kPa} = 14.2724 - \frac{2945.47}{t / ^\circ C + 224.00}
\]
Example cont.

<table>
<thead>
<tr>
<th>T</th>
<th>$a_{12}$</th>
<th>$P_{2}^{\text{sat}}$</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<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>

Answer (point b)
Bubble point calculation using relative volatility

**Definition of relative volatility:**
\[ \alpha_i = \frac{K_i}{K_{ref}} = \frac{y_i}{x_i} \]

**Solve for \( y_i \):**
\[ y_i = \alpha_i x_i K_{ref} \]

**Sum:**
\[ \sum_i y_i = 1.0 = \sum_i (\alpha_i x_i) K_{ref} \]

**Solve for \( K_{ref} \):**
\[ K_{ref} = \frac{1}{\sum_i \alpha_i x_i} \]

**Algorithm:**
given a solution composition (\( x_i \) values), find relative volatilities (\( \alpha_i \) values), then
1. guess \( T_{initial} \)
2. calculate \( K_{ref} \)
3. find \( T = T_{bp} \) corresponding to \( K_{ref} \)

Ex.: Finding \( T_{bp} \) using relative volatilities

*Find the bubble point of a mixture of n-pentane (\( x_P = 0.3 \)), n-hexane (\( x_X = 0.3 \)) and n-heptane (\( x_H = 0.4 \)), at 1 atm total pressure. Find the composition of the first vapor bubble.*
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Example cont.

Find Tbp corresponding to KP = 2.0 (read from DePriester Chart):

\[ Tbp = 58 \, ^\circ C \]

\[ y_P = 0.3(1)(2.0) = 0.60 \]

\[ y_i = \alpha_i x_i K_{ref} \]

\[ y_X = 0.3(0.43)(2.0) = 0.26 \]

\[ y_H = 0.4(0.16)(2.0) = 0.14 \]

\[ \sum_i y_i = 1 \]

Check:

Flash separation

- Another type of vapor-liquid equilibrium problem, and one that is more important for mass balances for designing separation equipment, is computing the two-phase equilibrium state when VLE either a liquid of known composition is partially vaporized or a vapor is partially condensed as a result of a change in temperature and/or pressure. This is referred to as a flash calculation.

- The term flash arises from the fact that if the pressure is suddenly lowered (or the temperature raised) on a mixture that is at its boiling temperature, it will flash-vaporize; that is, there will be a sudden partial vaporization of the liquid.

- The partial vaporization or partial condensation problem is somewhat more difficult to solve than bubble point and dew point calculations for the following reason:

- In a bubble point calculation an infinitesimal amount of vapor is produced, so the liquid composition is that of the original mixture; and

- In a dew point calculation, an infinitesimal amount of liquid forms, so the vapor composition is that of the original mixture.
Flash separation

- A liquid at a pressure equal to or greater than its bubble point pressure "flashes" or partially evaporates when the pressure is reduced producing a two-phase system of vapor and liquid in equilibrium.
- Flash calculation refers to any calculation of the quantities and compositions of the vapor and liquid phases making up a two-phase system in equilibrium at known T, P, and overall composition.
- Consider a system containing 1 mol with overall composition \( z_i \) (given) \( L \) the moles of liquid, \( V \) the moles of vapor

\[
1 = L + V \quad \text{(A)}
\]

\[
z_i = x_iL + y_iV \quad i = 1, 2, ..., N \quad \text{(B)}
\]

**Eq. (A) \times z_i**

\[
z_i = z_i L + z_i V \quad \text{(C)}
\]

**Eq. (B) – Eq. (C)**

\[
L \left( z_i - x_i \right) = V \left( y_i - z_i \right) \quad \text{Lever rule}
\]

- Substituting \( x_i = y_i/K_i \)

\[
y_i = \frac{z_iK_i}{1 + V(K_i - 1)} \quad i = 1, 2, ..., N
\]

- Because \( \sum y_i = 1 \)

\[
\sum_i \frac{z_iK_i}{1 + V(K_i - 1)} = 1
\]
Flash separation

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

Example

Example 10.5 acetone (1) / acetonitrile (2) / nitromethane (3)

$T = 80^\circ\text{C}$  $P = 110$ kPa and $z_1 = 0.45$  $z_2 = 0.35$  $z_3 = 0.20$
Because $P_{\text{dew}} < P < P_{\text{bubl}}$, the system is in the two-phase region, the mixture with the composition $z_i$ is in two-phase region $P$.

$$P = P_{x_i} = P_{y_i} = K_{z_i}$$

$$K_1 = \frac{195.75}{110} = 1.7795$$
$$K_2 = 0.8895$$
$$K_3 = 0.4575$$

The function is only of $T$ for ideal solution.

$$15425.01 = 4575.020.0 - 1105.01$$

Solving by trial and errors.

Example Cont.

Flash separation

$V = 0.7364 \text{ mol L}$

$= 0.2636 \text{ mol}$

$$y_1 = 0.5087$$
$$y_2 = 0.3389$$
$$y_3 = 0.1524$$

$$x_1 = 0.2859$$
$$x_2 = 0.3810$$
$$x_3 = 0.3331$$

Example Cont.