Chapter 10
Vapor/Liquid Equilibrium

- Previous chapters dealt with pure substances or with constant composition mixtures (air).

- But in chemical reactions and number of industrially mass-transfer operations the composition changes are the desired outcome. (Process such as distillation, absorption and extraction bring phases of different composition into contact).

- In such process. The extent of phase change and the rate of mass transfer depend on the departure of the system from the equilibrium.

- For quantitative treatment of mass transfer the equilibrium T, P and phase composition must be known.

- Two simple formulations that allow calculation of T, P and phase compositions for systems in vapor/liquid systems:
  
  - Raoults Law: Valid for systems at low to moderate pressure and systems of chemically similar species.
  - Henerys Law: Any species present at low concentration. Limited to low to moderate pressure.

- A modification of Raoults law (removes the restriction of chemically similar species) is treated in section 10.5.

- Finally, in section 10.6, calculations based on equilibrium ratio of K-values are considered.
10.4 Simple Models for a Vapor/Liquid Equilibrium

- **The goal is to find by calculation the T, P and compositions of phases in equilibrium.**

- **Raoult’s Law:**
  
  Two major assumptions:
  
  - The vapor phase is an ideal gas.
  - The liquid phase is an ideal solution (11.8).

- It means:
  
  - Raoult’s law can apply only for low to moderate pressures.
  - Raoult’s law can apply only when the species that comprise the system are chemically similar.

- **Ideal solution:** Approximated by liquid phases where molecular species are not too different in size and are of the same chemical nature.

  Example: Mixture of isomers such as ortho-, meta-, para- xylene.  
  Or adjacent members of homologues series: n-hexane/n-heptane  
  Ethanol/propanol  
  Benzene/toluene.

- Mathematical Expression:

  \[
  y_i P = x_i P_{i \text{ sat}} \quad (i = 1,2,\ldots,N) \tag{10.1}
  \]

  Where:
  
  - \( y_i \) = Vapor-phase mole fraction.
  - \( x_i \) = Liquid-phase mole fraction.
  - \( P_{i \text{ sat}} \) = Vapor pressure of pure species \( i \) at the \( T \) of the system.
  - \( y_i P \) = Partial pressure of species \( i \).

- **Limitation:** It can be applied only to a species for which vapor pressure is known.

- Vapor pressure given by empirical equations such as **Antoine equation**, where \( T \) is required.  
  This requires that the species “sub-critical” i.e. that the temperature of application be below the critical temperature of the species.
• Dew point and bubble point calculations with Raoult’s law:

  - **Bubl P:** Calculate \( y_i \) and \( P \), given \( x_i \) and \( T \).
  - **Dew P:** Calculate \( x_i \) and \( P \), given \( y_i \) and \( T \).
  - **Bubl T:** Calculate \( y_i \) and \( T \), given \( x_i \) and \( P \).
  - **Dew T:** Calculate \( x_i \) and \( T \), given \( y_i \) and \( P \).

• **Bubble point:** First bubble forms.

• **Dew point:** Liquid droplet remains.

• General procedure:

\[
\sum y_i = 1
\]

Then equation 10.1 becomes
\[
P = \sum x_i P_i^{sat}
\]  
(10.2)

Applied for Bubble point calculations where the vapor phase compositions are unknown.

For a binary system with
\[
x_2 = 1 - x_1
\]
\[
P = P_2^{sat} + (P_1^{sat} - P_2^{sat}) x_1
\]

Also 10.1 may be solved for \( x_i \) with
\[
\sum x_i = 1
\]
\[
P = 1/\sum y_i P_i^{sat}
\]  
(10.3)

Applied for Dew point calculations where liquid phase compositions are unknown.
Ex. 10.1

Binary system: acetic acid (1)/acetone (2)

Vapor pressures for the free species by Antoine equation:

\[
\ln P_v / kPa = 14.2724 - \frac{334.97}{T/\text{K}} - 2.24
\]

\[
\ln P_v / kPa = 14.2033 - \frac{357.04}{T/\text{K}} - 2.09
\]

@ Prepare a graph showing P vs X1 & P vs X2 for a temp of 75°C

@ Solve:

**Bulke P Calc.**

From known values of (X1, X2) we calculate the bulb’s vapor content.

\[ P = X_1 P_{v1} + (1 - X_1) P_{v2} \]

At 75°C, vapor pressure from the given Antoine equation

\[ P_1 = 83.21 \text{ kPa} \]
\[ P_2 = 41.98 \text{ kPa} \]

Now calculate P for any value of X1 between 0 & 1

Equation (A) for X1 = 0.6

\[ P = 41.98 + (83.21 - 41.98)(0.6) = 66.72 \text{ kPa} \]

From 10.1:

\[ y_1 = \frac{x_1 P_{v1}}{P} = \frac{(0.6)(83.21)}{66.72} = 0.7483 \]

These results mean that at 75°C & 1 atm, a mixture containing 60 mole percent acetic acid (1) & 40 mole percent acetone (2) is in equilibrium with a vapor containing 74.83% acetic acid (1) & 25.17% acetone (2) at a pressure of 66.72 kPa.

Based on similar calculations, we can prepare P-X, P-y diagrams.
$P_{x_1}$: Sat’d liquid.
$P_{y_1}$: Sat’d vapor.
Above $P_{x_1}$: Sub cooled liquid.
Below $P_{y_1}$: Superheated vapor.

Between $P_{x_1}$ & $P_{y_1}$ two phase region.

Lines meet at edges of the diagram: $P_{x_1}^{\text{sat}}$ and $P_{y_1}^{\text{sat}}$.

- **Point a**: sub cooled liquid mixture 60 mol\% & 40 mol\% at 75°C.
- Reduce pressure slowly so that system is always in equilibrium until point b.
- **Point b**: Sat’d liquid on the edge of vaporization.
- Further reduce the pressure till point b’, bubble of vapor appears.
- Points b and b’ are the equilibrium state $@ x_1 = 0.6$, $P = 66.72$, and $y_1 = 0.7483$(as we did calculated)
- **Point b is a bubble point**, $P_{x_1}$ line is the locus of bubble points.
- As pressure reduced, vapor increase and liquid decrease following the two paths b’c and bc-.
- Finally, approach point C where only a droplet of liquid remains. C is a dew point, $P_{y_1}$ line is the locus of dew points.
- **Point c-** read from the graph or calculated.
DEW P calculation: Calculate $x_1$ and $P$, given $y_i$ and $T$

$T = 75^\circ C, y_1 = 0.6$ 

Find $x_1$ and $P$.

By eqn (10.3)

$$P = \frac{1}{\frac{\alpha_1 P_{1sat}}{y_i} + \frac{\alpha_2 P_{2sat}}{y_i}}$$

for $y_i = 0.6$ and $T = 75^\circ C$

$$P = 59.74 \text{ kPa}$$

By eqn (10.11)

$$x_1 = \frac{y_i P}{P_{1sat}} = 0.4308$$

This is the liquid phase composition at $T_{1sat}$.

Here $P$ is fixed and temp vary with $x_i$ and $y_i$.

* No direct calc. of $T_{i}$ but through the vapor pressure.

For a given $P$, temp. is bounded between the two sat. temp. $T_1^{sat}$ and $T_2^{sat}$.

(They are the temp. which these species vapor pressure $= 0$)

For the present system, these temp. are calculated from Antoine's law.

$$T_i^{sat} = \frac{B_i}{A_i - \ln P} - C_i$$

For $P = 70 \text{ kPa}$

$$T_1^{sat} = 69.84^\circ C \quad \text{and} \quad T_2^{sat} = 89.58^\circ C$$

Prepare $T-x_i-y_i$ diagram:

- Select values of $T$ between these two temp. say $78^\circ C$.
- Calculate $P_{1sat}$ and $P_{2sat}$ for these temp. (Antoine eqn)
- Evaluate $x_1$ by eqn (A)

$$x_1 = \frac{P - P_{2sat}}{P_{1sat} - P_{2sat}}$$

For example @ $78^\circ C$

$$P_{1sat} = 59.76 \text{ kPa} \quad \text{and} \quad P_{2sat} = 46.84 \text{ kPa}$$
Constant pressure heating process:
- **Point a**: Sub cooled liq. of a composition of 60% acetonitrile.
- **Temp. increase** as a result of heating from a to b.
- **Point b**: first bubble of vapor appears. **Bubble point**. t-\(x_1\) is the locus of bubble points.
Bubl T calculation: Calculate $y_i$ and $T$, given $x_i$ and $P$.

P= 70 kpa, $x_1= 0.6$  
Find $y_1$ and $P$.  \textbf{[Iteration]}

- From eq. (10.2) write $P = P_2^{\text{sat}}(x_1(P_1^{\text{sat}}/P_2^{\text{sat}}) + x_2)$ \textbf{A}
- Solve for $P_2^{\text{sat}}$, defining $\alpha = P_1^{\text{sat}}/P_2^{\text{sat}}$
- $P_2^{\text{sat}} = P/x_1\alpha + x_2$ \textbf{B}
- $\ln \alpha = \ln (P_1^{\text{sat}}/P_2^{\text{sat}})$ \textbf{=} $\ln P_1^{\text{sat}} - P_2^{\text{sat}}$ \textbf{C}
- From Antoine equation $\ln \alpha = 0.0681 - 2,945.47/t + 224 + 2,972.64/209$
- $\alpha$ is a weak function of $t$.

\textbf{Iteration procedure:}
1- Calculate $P_2^{\text{sat}}$ from equation \textbf{B} with the current value of $\alpha$. (From part a @ 75$^\circ$C).
2- Calculate $t$ from Antoine equation for species 2:
   \[ t = 2,972.64/(14.2043-\ln P_2^{\text{sat}}) - 209 \]
3- Find a new value of $\alpha$ by equation \textbf{C}.
4- Return to the initial step and iterate to converge for final value of $t$.

The result is $t = 76.42^\circ$C (Temp. of points b and b').
From Antoine equation $P_1^{\text{sat}} = 87.17$ kpa.

From 10.1 b' composition:
\[ y_1 = x_1 P_1^{\text{sat}}/P = 0.6 \times 87.17/70 = 0.7472 \]

\textbf{Vaporizing a mixture at constant P, unlike vaporizing a pure species DOES NOT occur at constant temperature.}

As heating continue beyond b, temp raises and the amount of vapor increases. During this process, vapor and liquid compositions change as in path b–c and bc–.

- Dew point is reached at c where last droplet of liquid disappears (Dew point), $t$-$y_1$ is locus of dew points.
Dew T calculation: Calculate $x_i$ and $T_i$ given $y_i$ and $P$.

$P = 70$ kpa, $y_i = 0.6$ Find $x_i$ and $T_i$. \[ \text{[Iteration]} \]

$$\alpha = \frac{P_1^{\text{sat}}}{P_2^{\text{sat}}}$$

$$P_1^{\text{sat}} = P(y_1 + y_2\alpha)$$

Same iteration procedure as before but based on $P_1^{\text{sat}}$ instead of $P_1^{\text{sat}}$ with

$$t = \frac{2,972.64}{(14.2424 - \ln P_1^{\text{sat}})} - 224$$

The result is $t = 79.58^\circ\text{C}$ (Temp. of points $c$ and $c'$).

From Antoine equation $P_1^{\text{sat}} = 96.53$ kpa.

From 10.1 b composition:

$$x_1 = \frac{y_1 P}{P_1^{\text{sat}}} = 0.6 \times \frac{70}{96.53} = 0.4351$$

Temperature raises from $76.42^\circ\text{C}$ to $79.58^\circ\text{C}$ during the vaporization step from point $b$ to $c$.

Continue heating to super heated at point $d$. 
• **Henry’s Law:**
  - Raoult’s law requires $P_{i}^{\text{sat}}$ value at application temperature.
  - For species whose critical $T$ is less than the application temperature, this is not appropriate.
  - For example, **air dissolved in water** at equilibrium. (Air $T_{c} = 132.2^\circ K = -140.95^\circ C$ is much lower than $25^\circ C$).
  - Use Henry’s law for **dilute solute in the liquid phase** (liq. Mole fraction $< 0.01$ in system).

  - **Henry’s law:** The partial pressure of the species in the vapor phase is directly proportional to its liquid phase mole fraction.
  
  $\begin{align*}
  y_i P &= x_i \mathcal{H}_i \\
  \text{(10.4)}
  \end{align*}$

  Where, $\mathcal{H}_i$ from experiment (table 10.1) values at $25^\circ C$.

  - Examples: Removing Ammonia from air stream containing 2% Ammonia to become odorless.
  - $\text{CO}_2 + \text{Water}$

**Table 10.1: Henry’s Constants for Gases Dissolved in Water at 25$^\circ$C**

<table>
<thead>
<tr>
<th>Gas</th>
<th>$\mathcal{H}$/bar</th>
<th>Gas</th>
<th>$\mathcal{H}$/bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>1,350</td>
<td>Helium</td>
<td>126,600</td>
</tr>
<tr>
<td>Air</td>
<td>72,950</td>
<td>Hydrogen</td>
<td>71,600</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>1,670</td>
<td>Hydrogen sulfide</td>
<td>550</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>54,600</td>
<td>Methane</td>
<td>41,850</td>
</tr>
<tr>
<td>Ethane</td>
<td>30,600</td>
<td>Nitrogen</td>
<td>87,650</td>
</tr>
<tr>
<td>Ethylene</td>
<td>11,550</td>
<td>Oxygen</td>
<td>44,380</td>
</tr>
</tbody>
</table>
EX 16.2

\[ \text{CO}_2 \text{ and } \text{H}_2\text{O} \]

\[ x_1 + x_2 = ? \text{ in soda-lime} \]

\[ \Gamma = \frac{\rho}{\mu} \text{ on } 10^\circ \text{C} \]

\[ \text{H}_2\text{O} = 990 \text{ bar} \text{ at } 10^\circ \text{C} \]

So:

\[ \text{CO}_2 (1) \text{ and } \text{H}_2\text{O} (2) \]

Henyey law for \( \text{CO}_2 \Rightarrow \gamma_1 = \Lambda \frac{\rho}{\mu} \]

\& Rownt's law \( \text{H}_2\text{O} \Rightarrow \gamma_2 = 1 \frac{\rho}{\mu} \]

\[ \Rightarrow \frac{\rho}{\mu} = \frac{x_1}{\Lambda} + \frac{x_2}{\mu} \]

\[ \text{Assume } x_1 = 0.01 \text{ (vap. law)} \]

\[ \Lambda = 990 \text{ bar (given)} \]

\[ \mu = 0.1227 \text{ bar } \text{(steam table at } 10^\circ \text{C)} \]

\[ \Rightarrow \frac{\rho}{\mu} = (0.01)(990) + (0.99)(0.1227) = 9.91 \text{ bar} \]

\[ \Rightarrow \text{ use in Henyey's law to find new value of } x_1 \]

\[ \gamma_1(0.01) \text{ becomes } \frac{x_1}{\Lambda} = \frac{9.91}{990} = 0.01 \]

\[ \text{Confirm original assumption.} \]

\[ \text{By Rownt's law } \gamma_2(0.1) \text{ for species (2)} \]

\[ \gamma_2 = \frac{x_2}{\mu} = \frac{(0.99)(0.0012)}{0.1227} = 0.0012 \]

\[ y_2 = 1 - \gamma_2 = 1 - 0.0012 = 0.9988 \]

\( \text{Vapor phase is nearly pure } \text{CO}_2 \text{ as assumed).} \]
10.5 VLE by Modified Raoult’s Law

- **Deviation from solution ideality.**

\[ y_i P = x_i \gamma_i P_i^{\text{sat}} \quad (i = 1, 2, \ldots, N) \]  

Where \( \gamma_i \) = **Activity coefficient**.

- It is function of \( T \) and liquid composition and based on experiments. (12.1 give correlations to calculate \( \gamma \)).

- As a result, bubble point and dew point calculations are more complex.

- In this chapter \( \gamma \) values are assumed known.

- General solution:

\[
\begin{align*}
\sum y_i &= 1 \\
P &= \sum x_i \gamma_i P_i^{\text{sat}}
\end{align*}
\]  

Also you can solve for \( x_i \) from 10.5.

\[
\begin{align*}
\sum x_i &= 1 \\
P &= 1/ \sum y_i \gamma_i P_i^{\text{sat}}
\end{align*}
\]
EX 10.3  Given: Corr for azeotropic mixture.

\[ \ln y_i = A x_i^2 \quad \ln x_i = A x_i^2 \quad A = 2.771 - 0.00525 T \]

Antoine eqn for vapor press:

\[ \ln p_v = \text{some expression} \]

\[ \ln p_v = \text{some expression} \]

\[ T \text{ in } K, \quad p \text{ in atm, } x \text{ in } 0.0 \text{ to 1.0} \]

\[ \text{Calculate:} \]

\[ \text{1. P} \text{ is} \ y_i \text{ for } T = 318.15 \text{ K} \quad x_i = 0.25 \quad \text{(bub. P calc.)} \]

\[ \text{2. P} \text{ is} \ y_i \text{ for } T = 0.6 \quad x_i = 0.6 \quad \text{(deo. P calc.)} \]

\[ \text{3. T} \text{ for} \ \bar{p} = 101325 \text{ KPa} \quad x_i = 0.85 \quad \text{(bub. T calc.)} \]

\[ \text{4. T} \text{ for} \ \bar{p} = 101325 \text{ KPa} \quad y_i = 0.44 \quad \text{(deo. T calc.)} \]

\[ \text{5. The azeotropic pressure, } \bar{p} \text{, and the azeotropic composition, } x \text{, for } T = 318.5 \text{ K.} \]

\[ \text{After going through the above,} \quad \text{we get:} \]

Solution:

\[ \text{6. Bulb P Calculation.} \quad T = 318.15 \text{ K} \quad \text{Antoine eqn} \]

\[ \Rightarrow \quad \bar{p}_{\text{calc}} = 44.51 \quad \bar{p}_{\text{calc}} = 65.64 \text{ KPa} \]

\[ \text{7. Azeotropic Corr.} \quad A = 2.771 - (0.00525)(318.15) = 1.107 \]

\[ y_i = \exp \left( A x_i^2 \right) = \exp \left( (-1.107)(0.76^2) \right) = 0.28 \]

\[ y_i = \exp \left( A x_i^2 \right) = \exp \left( (1.075)(0.15^2) \right) = 0.72 \]

\[ \text{8. From Eqn (10.6) find } \bar{p} \]

\[ \bar{p} = \frac{E x_i \bar{p}}{8}; \quad \bar{p}_{\text{calc}} = (10.6) \]

\[ \bar{p} = (0.28)(1.26)(49.59) + (0.35)(1.075)(65.64) = 73.5 \text{ KPa} \]

\[ \text{9. From Eqn (10.5) find } y_i \]

\[ y_i = \frac{A x_i \bar{p}}{P}; \quad y_i = 0.282 \quad y_i = 0.728 \]
DEW point calculation

\[ y_1 = 0.6 \quad T = 318.15 K \]

1. The same as an azeo.
2. All vapor & liquid are the same.

Here, liquid phase composition \( X_1 = ?? \) unknown, but we need it for \( P \) calculation. Iterative procedure is required.

1. Initial value \( X_1 = X_2 = 1.0 \)
2. Calculate \( P \) by eqn (10.3)
   \[ P = \frac{1}{\frac{y_1}{X_1} P_{sat} + \frac{y_2}{X_2} P_{sat}^{300}} \]
3. Calculate \( X_1 \) by eqn (10.5)
   \[ X_1 = \frac{y_1 P}{X_1 P_{sat}^{300}} \]
   Then \( X_2 = 1 - X_1 \)
4. Recalculate activity coeff., \( \delta \), to the first step, continue
   \[ y_1 = \exp(\alpha X_1) \quad \delta_2 = \exp(\alpha X_1^2) \]
   to convergence

After going through this process,

\[ P = 62.28 \text{ kPa} \quad x_1 = 0.8169 \quad y_1 = 1.0378 \quad y_2 = 2.0935 \]
BUBL T Calculation

1. Given Antoine eqn for the spec. temp.
   \[ T_{1,\text{sat}} = \frac{B_1}{A_1 - \ln P} - C_1 \]

2. P = 101.33 kPa (given)
   \[ T_{1,\text{sat}} = 337.91 \quad T_2 = 330.82 \text{ K} \]

*Initial T is found by calculating a mole-fraction-weighted average of these values.*

\[ x_1 \text{ Antoine} T = (0.85)(337.91) + (0.15)(330.82) = 336.57 \text{ K} \]

2. Iterative Procedure start:
   - For the current value of T find \( A \), \( \beta_1 \), \( \beta_2 \) and \( \alpha = \frac{P_{\text{sat}}}{P} \) from the given eqns.

3. Find new value for \( P_{\text{sat}} \) from eqn (1.6) written as
   \[ P_{\text{sat}} = \frac{P}{x_1 \beta_1 + x_2 \beta_2} \]

4. Find a new value for T from Antoine eqn for species 2
   \[ T = \frac{B_1}{A_1 - \ln P_{\text{sat}}} - C_1 \]

5. Return to the initial step (2), iterate to convergence on value for T.
   \[ T = 331.20 \text{ K} \quad P_{\text{sat}} = 55.24 \text{ kPa} \quad P = 48.73 \]

\[ A = 1.0328 \quad B_1 = 1023.6 \quad B_2 = 2.1182 \]

The Vapor-Phase mole fraction \( y_1 = \frac{x_1 P_{\text{sat}}}{P} = 0.67 \quad y_2 = 1 - y_1 = 0.33 \)
DEW T calculation

\[ p = 101.33 \text{ kPa} \]

Assume \( T = 0 \text{ K} \) and \( x_1 = x_2 = 0.5 \).

The initial value for the unknown component found as mole-fraction weighted average of phase values:

\[ \frac{x_1 p_1 + x_2 p_2}{x_1 p_{1c} + x_2 p_{2c}} \]

Assume \( T = 0 \text{ K} \) and \( x_1 = x_2 = 0.5 \).

The initial value for the unknown component found as mole-fraction weighted average of phase values:

\[ \frac{x_1 p_1 + x_2 p_2}{x_1 p_{1c} + x_2 p_{2c}} \]

Evaluate \( A = \frac{p^{100} + \eta}{p^{100}} \) and \( x = \frac{p_{100}}{p_{200}} \) at the current value of \( T \) from Antoine equation.

\[ x_1 = \frac{310 p_1}{x_1 p_{1c}} \quad \text{and} \quad x_2 = 1 - x_1 \]

Calculate values of \( x_1 \) and \( x_2 \) from the given eqns.

Find a new value for \( T \) from Antoine equation given by:

\[ T = \frac{B_1}{A_1 - ln p_{100}} - C_1 \]

Return to the initial step and iterate with the current values of \( x_1 \) and \( x_2 \) until the process converges on a final value of \( T \).

Final values:

\[ T = 326.7 \text{ K} \]
\[ p_{100} = 64.63 \text{ kPa} \]
\[ p_{200} = 20.39 \text{ kPa} \]
\[ A = 1.0524 \]
\[ x_1 = 0.1825 \]
\[ x_2 = 0.2532 \]
\[ x_1 = 0.4602 \]
\[ x_2 = 0.5398 \]
- (a): P-\(x_1\) (or bubble point curve) lies below the linear P-\(x_1\) relation characteristics of Raoult’s law.

- (b): P-\(x_1\) curve exhibits a minimum, when the negative departures from linearity become sufficiently large, relative to the difference between the two pure species vapor pressure. Also P-\(y_1\) curve has a minimum at the same point.

- (c): P-\(x_1\) (or dew point curve) lies above the linear P-\(x_1\) relation.

- (d): P-\(x_1\) curve exhibits a maximum, when the positive departures from linearity become sufficiently large, relative to the difference between the two pure species vapor pressure. Also P-\(y_1\) curve has a maximum at the same point.

- At this point,
  - \(x = y\)
  - Dew point and bubble curves are tangent to the same horizontal line.
  - For minimum pressure, the vapor and liquid phases in equilibrium have identical composition.

- This is called “Azetrope”.

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**Figure 10.8**  \(P_x y\) diagrams at constant \(T\): (a) tetrahydrofuran(1)/carbon tetrachloride(2) at 30°C; (b) chloroform(1)/tetrahydrofuran(2) at 50°C; (c) furan(1)/carbon tetrachloride(2) at 30°C; (d) ethanol(1)/toluene(2) at 65°C. Dashed lines: \(P_x\) relation for Raoult’s law.
- It means: *A boiling liquid of this composition produces a vapor of exactly the same composition as the liquid; therefore does not change in composition as it evaporate.*
  *NO SEPERATION of such a constant-boiling solution is possible by distillation.*

- **Negative departure** from linearity ≡ Stronger liquid phase intermolecular attractions between *unlike* than between like pairs of molecules.

- **Positive departure** from linearity ≡ Stronger liquid phase intermolecular attractions between *like* than between unlike pairs of molecules.
- t-x_1-y_1 diagram of data at constant P.

- This is more of interest because distillation process is carried out more nearly at constant P than constant temperature.

- Opposite to figure 10.8. (Azeotrope in opposite sides).
Figure 10.10: $y_x$ diagrams at 1(atm):
(a) tetrahydrofuran(1)/carbon tetrachloride(2);
(b) chloroform(1)/tetrahydrofuran(2);
(c) furan(1)/carbon tetrachloride(2);
(d) ethanol(1)/toluene(2).

- $x_1$-$y_1$ at constant pressure for the same systems.
- Point at which curve crosses the diagonal line of diagram is Azetrope ($x_1 = y_1$).
- (a) and (c) no azetropes.
- (b) and (d) azetrope across the diagonal.
There are two kinds of questions about azetrops:

1- Do we have azetrope at this given temperature for this given system?
2- What are azetropic pressure and azetropic compositions?

1- Do we have azetrope at this given temperature for this given system?

- Let Relative Volatility, \( \alpha_{12} = \frac{y_1}{x_1} \frac{x_1}{y_2} \) (10.8)
- At an Azetrope, \( y_1 = x_1 \), \( y_2 = x_2 \) and \( \alpha_{12} = 1 \)
- From modified Raoults’s law, eq’n (10.5):
  \[ \frac{y_1}{x_1} = \gamma_1 \frac{P_1^{sat}}{P} \]
- Substitute in 10.8,
  \[ \alpha_{12} = \frac{\gamma_1 P_1^{sat}}{\gamma_2 P_2^{sat}} \] (10.9)
- Since \( \ln \gamma_2 = Ax_1^2 \) and \( \ln \gamma_1 = Ax_2^2 \) (given)
- Then, When \( x_1 = 0 \) \( \rightarrow \) \( \gamma_2 = 1 \) and \( \gamma_1 = \exp(A) \)
- And, When \( x_1 = 1 \) \( \rightarrow \) \( \gamma_1 = 1 \) and \( \gamma_2 = \exp(A) \)
- In these limits, substitute in 10.9,
  \[ (\alpha_{12})_{x_1=0} = \frac{P_1^{sat}}{P_2^{sat}} \exp(A) \] and \[ (\alpha_{12})_{x_1=1} = \frac{P_1^{sat}}{P_2^{sat}} \exp(A) \]
- For the temperature of interest, \( P_1^{sat} = 44.51 \) , \( P_2^{sat} = 65.64 \) kpa
- The limiting values of \( \alpha_{12} \) from the above equations;
  \( (\alpha_{12})_{x_1=0} = 2.052 \) Value of one limit > 1 and
  \( (\alpha_{12})_{x_1=1} = 0.224 \) Value of one limit < 1
- So Azetrope does exist.
- \( \alpha_{12} \) is a continues function of \( x_1 \) and must pass through the value of 1.0 at some intermediate composition.
2- What are azetropic pressure and azetropic compositions?

- Since for azetrope \( \alpha_{12} = 1 \)

Then eq’n 10.9 becomes, \( \frac{\gamma_{1}^{az}}{\gamma_{2}^{az}} = \frac{P_{2}^{sat}}{P_{1}^{sat}} = \frac{65.64}{44.51} = 1.4747 \)

- The difference between the correlation equations for \( \ln \gamma_1 \) and \( \ln \gamma_2 \) provides the general relation:

\[
\ln \frac{\gamma_1}{\gamma_2} = A x_2^2 - A x_1^2 = A (x_2 - x_1) (x_2 + x_1) = A (x_2 - x_1) = A (1 - 2 x_1)
\]

- \( \ln \frac{\gamma_1}{\gamma_2} = \ln 1.4747 = 0.388 \)

- Then \( 0.388 = A (1 - 2 x_1^{az}) \) \( \rightarrow x_1^{az} = 0.325 \)

- And \( \gamma_1^{az} = 1.657 \)

- With \( x_1^{az} = y_1^{az} \)

- \( P^{az} = \gamma_1^{az} P_1^{sat} = (1.657) (44.51) = 73.76 \text{ kpa, and} \)

- \( x_1^{az} = y_1^{az} = 0.325 \)
10.6 VLE from K-value correlations

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

K-value measure the tendency of species to favor the vapor phase.

\( K_i > 1 \) Species I exhibit a higher concentration in the vapor phase.

\( K_i < 1 \) Species I exhibit a higher concentration in the liquid phase.

Allowing elimination of one set of mole fractions x or y, two types of calculations result:

**Bubble point calculation:** \( y_i = k_i x_i \) and \( \sum y_i = 1 \)

Then \( \sum k_i x_i = 1 \)  \hspace{1cm} (10.13)

Find the set of K-values that satisfies equation 10.13

**Dew point calculation:** \( x_i = \frac{y_i}{k_i} \) and \( \sum x_i = 1 \)

Then \( \sum \frac{y_i}{k_i} = 1 \)  \hspace{1cm} (10.14)

Find the set of K-values that satisfies equation 10.14

- Figures 10.13 and 10.14 show monographs for the k-values of light hydrocarbons as function of T and P. They are prepared for average effect of compositions.
Ex. 10.4:

a- When system is at its dew point:
- Only an insignificant amount of liquid is present.
- The given mole fraction are values of \( y_i \).
- For the given \( T \), K-values depend on the choice of \( P \), by trial and error find the value for which equation 10.14 satisfied.
- Drew a line between the selected pressure and \( T=50^\circ F \) and find \( k \)-values.

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
\text{Species} & y_i & K_i & y_i/K_i & K_i & y_i/K_i \\
\hline
\text{Methane} & 0.10 & 20.0 & 0.005 & 13.2 & 0.008 & 16.0 & 0.006 \\
\text{Ethane} & 0.20 & 3.25 & 0.062 & 2.25 & 0.089 & 2.65 & 0.075 \\
\text{Propane} & 0.70 & 0.92 & 0.761 & 0.65 & 1.077 & 0.762 & 0.919 \\
\hline
\end{array}
\]

\[
\sum (y_i/K_i) = 0.828 \quad \sum (y_i/K_i) = 1.174 \quad \sum (y_i/K_i) = 1.000
\]

- Equation 10.14 satisfied when \( P=126 \text{ psia} \). This is the dew point \( P \). The dew compositions are given by the values of \( x_i \) listed in the last column.

b- The system is completely condensed, it is at its bubble point.
- The given mole fraction are values of \( x_i \).
- By trial and error find the value of \( P \) for which \( k \)-values satisfy equation 10.13.
- Drew a line between the selected pressure and \( T=50^\circ F \) and find \( k \)-values.

\[
\begin{array}{|c|c|c|c|c|c|c|}
\hline
\text{Species} & x_i & K_i & K_i x_i & K_i & K_i x_i \\
\hline
\text{Methane} & 0.10 & 5.60 & 0.560 & 5.25 & 0.525 & 5.49 & 0.549 \\
\text{Ethane} & 0.20 & 1.11 & 0.222 & 1.07 & 0.214 & 1.10 & 0.220 \\
\text{Propane} & 0.70 & 0.335 & 0.235 & 0.32 & 0.224 & 0.33 & 0.231 \\
\hline
\end{array}
\]

\[
\sum K_i x_i = 1.017 \quad \sum K_i x_i = 0.963 \quad \sum K_i x_i = 1.000
\]

- Equation 10.13 satisfied when \( P=385 \text{ psia} \). This is the bubble point \( P \). The bubble compositions are given by the values of \( y_i \) listed in the last column.
Flash Calculations

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-liquid in equilibrium.

Flash vaporization with V and L in equilibrium

- $L \equiv$ moles of liquid, with mole fraction $[x_i]$.  
- $V \equiv$ moles of vapor, with mole fraction $[y_i]$.  
- $Z_i \equiv$ over all mole fraction.  
- $L + V = 1$  
- $Z_i = x_i \ L + y_i \ V$

Combine equations to eliminate L and substitute with $x_i= y_i/ k_i$ then solve for $y_i$

$$y_i = Z_i \ k_i / 1 + V( k_i -1)$$  \hspace{1cm} (10.16)

Since $\sum y_i = 1$, then

$$\sum Z_i \ k_i / 1 + V( k_i -1) = 1$$  \hspace{1cm} (10.17)

The initial step for solving a P-T flash problem is to find the value of V that satisfies this equation.

Read Ex. 10.5
Flash calculations can also be made for light hydrocarbons with data from figures 10.13 and 10.14.

Ex. 10.6

- The given pressure (200 psia) between bubblepoint and dewpoint pressures as found in Ex.10.4.
- So the system consists of two phases.
- K-values from fig. 10.13.
- By trial and error find value of V for which equation 10.17 satisfied.

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
\text{Species} & z_i & K_i & y_i & y_i & y_i \\
& & & \text{for } V = 0.35 & \text{for } V = 0.25 & \text{for } V = 0.273 \\
\hline
\text{Methane} & 0.10 & 10.0 & 0.241 & 0.308 & 0.289 \\
\text{Ethane} & 0.20 & 1.76 & 0.278 & 0.296 & 0.292 \\
\text{Propane} & 0.70 & 0.52 & 0.438 & 0.414 & 0.419 \\
\hline
\end{array}
\]

\[
\begin{align*}
\Sigma y_i &= 0.957 & \Sigma y_i &= 1.018 & \Sigma y_i &= 1.000 & \Sigma x_i &= 1.000 \\
\end{align*}
\]

- Equation 10.17 satisfied when V=0.273
- The phase compositions are given in the last two columns.