Problem 33

\[ \frac{G^{E}}{RT} = 0.95 x_1 x_2 \]

\[ \frac{G^{E}}{RT} = \ln \gamma_1 = \left[ \frac{\partial (\ln (G^{E}/RT))}{\partial n_1} \right]_{T, P, n_2} \]

\[ = \frac{3}{\partial n_1} \left( 0.95 \frac{n_1}{\bar{n}} \cdot \frac{n_2}{\bar{n}} \right) \]

\[ = \frac{3}{\partial n_1} \left( 0.95 \frac{n_1 n_2}{n_1 + n_2} \right) \]

\[ = 0.95 n_2 \cdot \frac{3}{\partial n_1} \left( \frac{n_1}{n_1 + n_2} \right) \]

\[ = 0.95 n_2 \cdot \left[ -\frac{n_1}{(n_1 + n_2)^2} + \frac{1}{n_1 + n_2} \right] \]

\[ = 0.95 x_2 \left( 1 - x_1 \right) \]

\[ = 0.95 x_2^2 \]

\[ \frac{G^{E}}{RT} = \ln \gamma_2 \]

from \[ \frac{G^{E}}{RT} = \sum_{i} x_i \ln \gamma_i = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \]

\[ \ln \gamma_2 = \left( \frac{G^{E}}{RT} - x_1 \ln \gamma_1 \right) \cdot \frac{1}{x_2} \]

\[ = (0.95 x_2 - x_1 \cdot 0.95 x_2^2) \cdot \frac{1}{x_2} \]

\[ = 0.95 x_1 - 0.95 x_1 x_2 \]

\[ = 0.95 x_1^2 \]
From \( y_iP = y_iP_i^{\text{sat}} \) => modified Raoult's law

\[ y_iP = \sum y_i x_i P_i^{\text{sat}} = \gamma_1 x_1 P_1^{\text{sat}} + \gamma_2 x_2 P_2^{\text{sat}}, \text{ sir} \]

\[ P = \gamma_1 x_1 P_1^{\text{sat}} + \gamma_2 x_2 P_2^{\text{sat}} \]

Since we know \( \ln \gamma_1 \), and \( \ln \gamma_2 \), as a function of \( \gamma_1 \), and \( \gamma_2 \), we can calculate \( \gamma_1 \), and \( \gamma_2 \).

\[ P_{\text{Bubbling}} \text{ and } P_{\text{Rew}} \]

At \( x_1 = 0.5 \)

\[ \ln \gamma_1 = 0.2375 \quad \Rightarrow \gamma_1 = 1.268 \]

\[ \ln \gamma_2 = 0.2375 \quad \Rightarrow \gamma_2 = 1.268 \]

\[ P_{\text{Bubbling}} = (1.268 \times 0.5 \times 74.8) + (1.268 \times 0.5 \times 40.5) \]

\[ P_{\text{Bubbling}} = 76.3 \text{ kPa} \]

And \( y_1P = \gamma_1 x_1 P_1^{\text{sat}} \)

\[ y_1 = \frac{\gamma_1 x_1 P_1^{\text{sat}}}{P} = \frac{1.268 \times 0.5 \times 74.8}{76.3} \]

\[ y_1 = 0.66 \]
b) $y_1 = 0.5 \quad y_2 = 0.5 \quad y_1' = y_1 x_i P_i^{sat} \quad y_2' = y_2 x_i P_i^{sat}$

$z x_i = \sum y_i' \quad \frac{y_i'}{y_i^{sat} P_i}$

$p = \frac{1}{y_1' \frac{y_1}{y_1^{sat} P_1} + y_2' \frac{y_2}{y_2^{sat} P_2}}$

We need $y_1$ and $y_2$, but since we don't know $y_2$, we need to do the calculations iteratively.

- First assume $y_1 = 1$, $y_2 = 1$, then calculate $P_{rew}$ using $e$
- With that value of $P_{rew}$, use $x_1 = \frac{y_1 P_{rew}}{y_1^{sat} P_1}$ and to calculate $x_1$ and $x_2$
- With these $x_1$ and $x_2$, recalculate $y_1$ and $y_2$
- Repeat until converge

<table>
<thead>
<tr>
<th>$y_1$</th>
<th>$y_2$</th>
<th>$P_{rew}$</th>
<th>$x_1$</th>
<th>$x_2$</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>53.7</td>
<td>0.337</td>
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<td>1.52</td>
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<tr>
<td>after ~ 6 steps</td>
<td>1.745</td>
<td>1.054</td>
<td>65.3</td>
<td>0.235</td>
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</table>

$P_{rew} = 65.3 \text{ kPa}$

$x_1 = 0.235$

* or use $\frac{y_1'}{y_2'} = \frac{y_1 x_i P_i^{sat}}{y_2 x_2 P_2^{sat}}$ to eliminate $P$ and solve
c) At azeotrope, \( y_1 = x_1 \) and \( y_2 = x_2 \)

and \( p_{\text{bubble}} = p_{\text{ dew}} \)

\[
\begin{align*}
\gamma_1 x_1 p_1^{\text{sat}} + \gamma_2 x_2 p_2^{\text{sat}} &= \frac{1}{\gamma_1 x_1 p_1^{\text{sat}}} + \frac{y_2}{\gamma_2 x_2 p_2^{\text{sat}}} \\
\gamma_1 x_1 p_1^{\text{sat}} + \gamma_2 (1-x_1) p_2^{\text{sat}} &= \frac{1}{\gamma_1 x_1 p_1^{\text{sat}}} + \frac{(1-x_1)}{\gamma_2 x_2 p_2^{\text{sat}}}
\end{align*}
\]

with \( \ln y_1 = 0.95 (1-x_1)^2 \) and \( \ln y_2 = 0.95 x_1^2 \)

we have an equation that has only \( x_1 \) as an unknown

solve this equation to get \( x_1 = 0.857 \)

\[
\begin{align*}
\text{Composition:} & \quad y_1 = x_1 = 0.857 \\
& \quad y_2 = x_2 = 0.143
\end{align*}
\]

and

\[
p = \gamma_1 x_1 p_1^{\text{sat}} + \gamma_2 x_2 p_2^{\text{sat}}
\]

\[
p = 81.4 \text{ kPa}
\]

*or you can use \( \frac{y_1 R}{y_2 R} = \frac{\gamma_1 x_1 p_1^{\text{sat}}}{\gamma_2 x_2 p_2^{\text{sat}}} \) to eliminate \( p \), ar
Problem 34

a) \( \frac{C^F}{RT} \)

Following procedures used in problem 33

\[
\ln \gamma_1 = 0.64 x_2^2 \\
\ln \gamma_2 = 0.64 x_1^2 
\]

from modified Raoult's law \( y_i P = x_i x_i P_i^{sat} \)

\[
P_{bubble} = \sum x_i x_i P_i^{sat} = y_1 x_1 P_1^{sat} + y_2 x_2 P_2^{sat}
\]

Using Antoine equation \( \ln P^{sat} = A - \frac{B}{T+C} \) \( P^{sat} \) in kPa

For acetone (1) \( A = 14.3916 \) \( B = 2795.82 \) \( C = 230 \)

For methanol (2) \( A = 16.5938 \) \( B = 3644.3 \) \( C = 239.76 \)

At 50°C \( P_1^{sat} = 82.0 \) kPa \( P_2^{sat} = 55.5 \) kPa

To construct Pxy diagram

- Pick a value of \( x_1 \), then calculate \( y_1 \) and \( y_2 \)
- Calculate \( P_{bubble} \) using eqn. (1B)
- Using eqn (1A), calculate \( y_1 = \frac{y_1 x_1 P_1^{sat}}{P_{bubble}} \), this mole fraction of acetone in the vapor that is in equilibrium liquid of composition \( x_1 \) at \( P = P_{bubble} \)
b) To construct a T-s diagram

- Set P at 75 kPa
- Pick a value of \( x_1 \)
- Using eqn (B) with \( P_{\text{base}} = 75 \text{ kPa} \)
calculate \( T \), since \( p_1^{\text{sat}} \) and \( p_2^{\text{sat}} \) are function by Antoine equations

- Knowing \( T \), hence \( p_1^{\text{sat}} \), we can calculate \( y_1 \) using
or you can pick \( T \), and get \( p_1^{\text{sat}} \) from Antoine eqns, then \( x_1 \)

(c)

```
Flow = V
Composition \( y_1 = ? \)
\( y_2 = ? \)
\( P = 100 \text{ kPa} \)
```

Flow = L
Composition \( x_1 = 0.5 \)
\( x_2 = 0.5 \)

Using
\[
P_{\text{base}} = x_1 p_1^{\text{sat}} + x_2 p_2^{\text{sat}}
\]

\[
100 = \exp(0.64 \cdot 0.5^2) \times 0.5 \times \exp\left[ \frac{41.3916 - 2749.82}{t + 239.76} \right]
+ \exp(0.64 \cdot 0.5^2) \times 0.5 \times \exp\left[ \frac{16.5933 - 3644.3}{t + 239.76} \right]
\]

solve this equation to get \( t = 55.6 \text{ °C} \)

\[
y_1 = \frac{x_1 p_1^{\text{sat}}}{P} = \frac{\exp(0.64 \cdot 0.5^2) \times 0.5 \times \exp\left[ \frac{41.3916 - 27}{t + 239.76} \right]}{100}
\]

\[\text{55.6}\]
Performing material balances on

Total  \[ F = V + L \]

Component 1  \[ 0.75 F = 0.58V + 0.5 L \]

\[ 0.75(V+L) = 0.58V + 0.5L \]

\[ 0.25L = -0.17V \]

\[ \frac{L}{V} = -0.68 \]

this is not possible as we have a negative flow, we want to flow in the V stream
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<th>Acetone (1)</th>
<th>Methanol (2)</th>
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<tr>
<td>B</td>
<td>2795.82</td>
<td>3644.3</td>
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<td>C</td>
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<td>239.76</td>
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<tr>
<td>t</td>
<td>50</td>
<td>50</td>
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<tr>
<td>P_{sat} (kPa)</td>
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<tr>
<th>x_1</th>
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<td>1.896</td>
<td>81.98</td>
<td>1.00</td>
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Problem 35

a) Henry’s law \[ y_i P = P_i = H_i x_i \]

\[ P_0 = 1 \text{ atm} \]

In 1 liter of \((C_4F_8)_3N\), we have 384 ml of \(O_2\) dissolved in assuming ideal gas \[ \frac{PY}{RT} = n \]

\[ \text{atm, } 25^\circ C \]

\[ n = \frac{PY}{RT} = \frac{1.01325 \times 10^5 \times 3.84 \times 10^{-6}}{8.314 \times 298} \]

\[ \text{J/mol K) (K)} \]

\[ = 0.0157 \text{ moles of } O_2 \]

we have \[ 1.833 \times 1000 = 1833 \text{ g of solvents in a liter} \]

ie. \[ \frac{1893}{3 \times 3(2 \times 4) + (11 \times 9) + 14} \]

\[ C \quad F \quad N \]

\[ H_o = \frac{P_o}{P_0} = \frac{1}{0.0157/0.0157 + 2.806} \]

\[ H_o = 180 \text{ atm} \]

b) In 1 liter of oxygenEL \[ \Rightarrow 0.2 \text{ liters of } (C_4F_8)_3N \]

0.3 liters of water

Air consists of \( \sim 20\% \text{ O}_2 \)

\[ \therefore \text{ oxygen partial pressure in air at 1 atm is} \]

\[ P_o = 0.2 \]
For \((\text{C}_4\text{F}_4)_3\text{N}\)

\[
\frac{\text{P}_{\text{O}_2}}{\text{H}_{\text{O}_2}} = \frac{0.2}{180} = 0.0011
\]

we have \(1323 \times 0.2 \times 1000 = 376.6 \text{ g} \) \((\text{C}_4\text{F}_4)_3\text{N}\)

or \(\frac{376.6}{671} = 0.561 \text{ moles of } (\text{C}_4\text{F}_4)_3\text{N}\)

hence we have \(0.0011 = \frac{n_{\text{O}_2}^{(\text{C}_4\text{F}_4)_3\text{N}}}{n_{\text{O}_2}^{(\text{C}_4\text{F}_4)_3\text{N}} + 0.561}\)

\[n_{\text{O}_2}^{(\text{C}_4\text{F}_4)_3\text{N}} = 0.000 \text{ mole}\]

For water

\[
\frac{\text{P}_{\text{O}_2}}{\text{H}_{\text{O}_2}} = \frac{0.2}{4.38 \times 10^2} = 4.57 \times 10^{-6}
\]

we have \(1 \times 0.8 \times 1000 = 800 \text{ g of water}\)

\(p = 1 \text{ g/mL}\)

or \(\frac{800}{18} = 44.44 \text{ moles of } \text{H}_2\text{O}\)

\[4.57 \times 10^{-6} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}} + 44.44}\]

\[n_{\text{H}_2\text{O}} = 0.000203 \text{ moles}\]

\[n_{\text{H}_2\text{O}} = 0.000624 + 0.000203 = 0.000827 \text{ moles}\]

At 1 atm, 25°C, this has volume \(V = \frac{nRT}{p} = \frac{0.000827 \times 8.314}{1.01325 \times 10} = \text{mL}\)
\[ V_{\text{dissolve}} = 20.2 \text{ ml} \]

C) For 1 litre of water

\[ \text{ie. } 1000 \text{ g H}_2\text{O} \quad \text{or} \quad \frac{1000}{18} = 55.56 \text{ moles of H}_2\text{O} \]

\[ 4.57 \times 10^{-4} = \frac{n_2}{n_2 + 55.56} \]

\[ n_2 = 0.00254 \text{ moles.} \]

At 1 atm, 25°C

\[ V^b = \frac{0.00254 \times 8.314 \times 298}{1.01325 \times 10^5} \times 10^6 \]

\[ V = 6.2 \text{ ml} \]