Problem 1: Assuming a mixture of n-pentane (nC_5) and n-heptane (nC_7) is ideal, draw vapour-liquid equilibrium diagrams for this mixtures at:

(a) Constant temperature of 50°C;

(b) Constant pressure of 1.013 bar.

Problem 2: (a) Estimate the bubble and dew point temperatures of a 25 mol-% n-pentane (nC_5), 45 mol-% n-hexane (nC_6) and 30 mol-% n-heptane (nC_7) mixture at 1.013 bar.

(b) Estimate the bubble and dew point pressures of this mixture at 73°C.

Problem 3: An ideal liquid mixture of 25 mol-% n-pentane (nC_5), 45 mol-% n-hexane (nC_6) and 30 mol-% n-heptane (nC_7), initially at 69°C and high pressure, is partially vaporised by isothermically lowering the pressure to 1.013 bar. Calculate the relative amounts of vapour and liquid in equilibrium and their compositions.

Problem 4: Assuming Raoult's law to apply to the system n-pentane (nC_5) and n-heptane (nC_7), determine the composition of the vapour phase, y_{nC_5} for $0.1 \leqslant x_{nC_5} \leqslant 0.5$ at 55°C and P at the arithmetic average of the saturation pressures of the pure species. The Antoine coefficients of the chemicals are A_{nC_5} = 13.7667, B_{nC_5} = 2451.88, C_{nC_5} = 232.014, A_{nC_7} = 13.8622, B_{nC_7} = 2911.26, C_{nC_7} = 216.432,

$$\ln P^{\text{sat}} = A - \frac{B}{T+C} \quad \text{with [P] = kPa and [T] = °C}$$

Problem 5: A process stream contains light species 1 and heavy species 2. A relatively pure liquid stream containing mostly 2 is obtained through a single-stage liquid/vapour separator. Specifications on the equilibrium composition are: x_1 = 0.002 and y_1 = 0.950. Assuming that the modified Raoult's law applies,

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

Determine T and P for the separator. Given the activity coefficients for the liquid phase,

$$\ln \gamma_1 = 0.93 x_2^2 \qquad \text{and} \qquad \ln \gamma_2 = 0.93 x_1^2$$

$$\ln P^{\text{sat}} = A - \frac{B}{T} \quad \text{with [P] = bar and [T] = K}$$

A_1 10.08, B_1 = 2572.0, A_2 = 11.63 and $B_2 = 6254.0$.

Problem 6: Determine the compositions of the gas and liquid phases of air in equilibrium with water at ambient conditions, 25°C and 1 atm. Given: Henry's constant for air dissolved in water at 25°C is 72950 bar.

Problem 7: For the acetone (Ket) / methanol (MetOH) system, a vapour mixture of z_{Ket} = 0.25 and z_{MetOH} = 0.75 is cooled to temperature T in the two-phase region and flows into a separation chamber at a pressure of 1 bar. If the composition of the liquid product is x_{Ket} = 0.175, calculate T and y_{Ket}. For liquid mixture, assume that

$$\ln \gamma_1 = 0.64 x_2^2 \qquad \text{and} \qquad \ln \gamma_2 = 0.64 x_1^2$$

For the Antoine equation,

$$\ln P_i^{\text{sat}} = A_i - \frac{B_i}{T + C} \quad \left([\text{P}] = \text{kPa and } [\text{T}] = {}^\circ\text{C} \right)$$

A_{Ket} = 14.3145, B_{Ket} = 2756.22, C_{Ket} = 228.060, A_{MetOH} = 16.5785, B_{MetOH} = 3638.27, C_{MetOH} = 239.50.

For **Problem 1:- Problem 3:**, use

$$\ln P_i^{\text{sat}} = A_i - \frac{B_i}{RT}$$

with [P] = bar and [T] = K, and

$$\begin{array}{lll} A_{nC_5} = 10.422 & A_{nC_6} = 10.456 & A_{nC_7} = 11.431 \\ B_{nC_5} = 26799 & B_{nC_6} = 29676 & B_{nC_7} = 35200 \end{array}$$

#25 Example 1 : nC_5 & nC_7
Problem 1
C_p ideal

$$\ln P_5^{sat} = 10.422 - \frac{26799}{RT} \qquad \ln P_7^{sat} = 11.431 - \frac{35200}{RT}$$

$[P]$: bar $\qquad R = 8.314\ J/(gmol.K)$

$[T]$: K

(a) $T = 50°C$

(b) $P = 1.013$ bar

Is this problem solvable? From Gibb's phase rule

$$\varphi = 2 + C - P = 2 + 2 - 2 = 2$$

With 2 dof, we can fix either T (part a) or pressure (part b) as one dof, and then for each liquid phase composition (second dof) calculate the equilibrium conditions.

(a) For $T = 50°C = 323.15K$ $\begin{cases} P_5^{sat} = 1.5639 \text{ bar} \\ P_7^{sat} = 0.1881 \text{ bar} \end{cases}$

To calculate the equilibrium pressure at each liquid pentane composition, x_5,

$P_i = x_i P_i^{sat}$

$P = P_1 + P_2 + \ldots = \sum x_i P_i^{sat}$

$$P(x_5) = x_5 P_5^{sat} + x_7 P_7^{sat} = x_5 P_5^{sat} + (1 - x_5) P_7^{sat}$$

$y_i P = x_i P_i^{sat}$

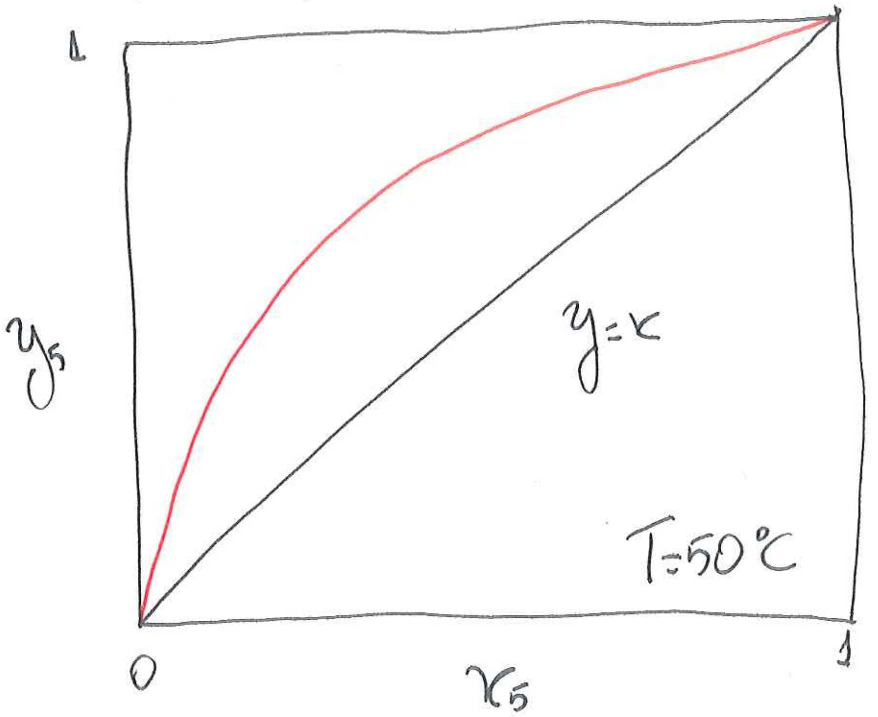
And for vapour composition

$$y_5 = \frac{x_5 P_5^{sat}}{P(x_5)}$$

With this equation

$$y_5 = \frac{x_5 P_5^{sat}}{x_5 P_5^{sat} + (1 - x_5) P_7^{sat}}$$

we can plot $x_5 \times y_5$ at $T = 50°C$



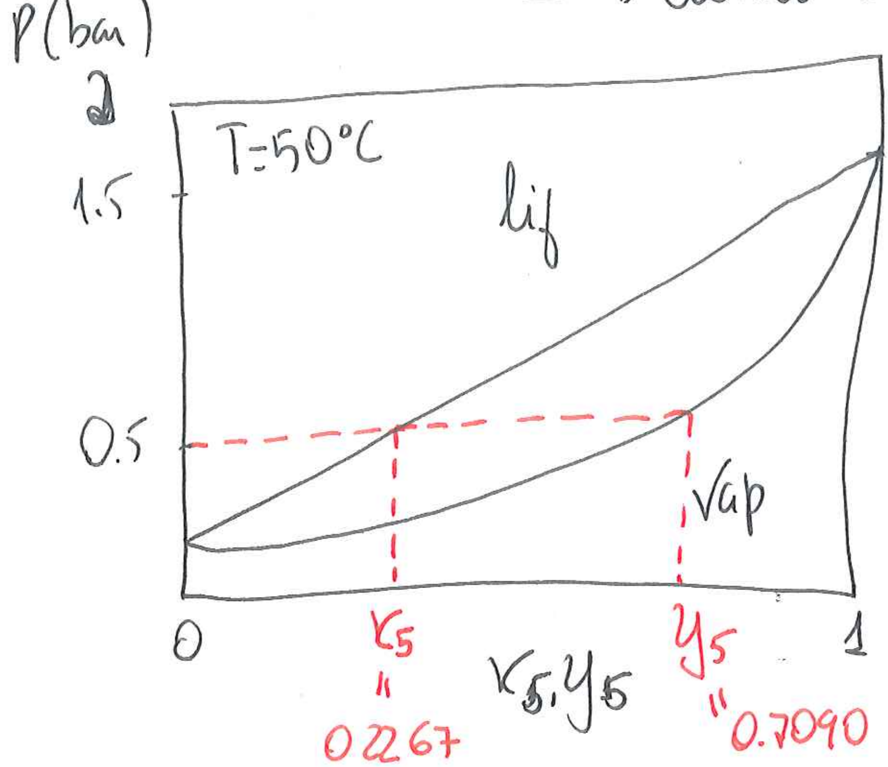
Alternatively we can plot $P \times (xy)_5$ using

$$y_5 = \frac{x_5 P_5^{sat}}{P}$$

$$P = x_5 P_5^{sat} + (1 - x_5) P_7^{sat} = P_7^{sat} + x_5 (P_5^{sat} - P_7^{sat})$$

$$x_5 = \frac{P - P_7^{sat}}{P_5^{sat} - P_7^{sat}} \rightsquigarrow$$

Given P
↳ calculate x_5
↳ calculate y_5



Eg: At P = 0.5 bar
↳ $x_5 = 0.2267$
↳ $y_5 = 0.7090$

At P = 0.80 bar
$y_5 = 0.8694$
$x_5 = 0.4447$

(b) Equilibrium temperature at each composition is not known
↳ P^{sat} are non-linear functions of T

$$x_5 P_5^{sat}(T) + x_7 P_7^{sat}(T) = x_5 P_5^{sat}(T) + (1-x_5) P_7^{sat}(T) = 1.013 \text{ bar}$$

↳ solve by iterative methods
↳ or for each $\underline{x_5}$ → initial guess for $\underline{T}$ until the left-hand side = 1.013 bar

$$F = x_5 P_5^{sat} + (1 - x_5) P_7^{sat} - 1.013 = 0$$

Iterative method for T

$$T^{i+1} = T^{i} - \frac{F(T^{i})}{F'(T^{i})}$$

$$F'(T) = \frac{dF(T)}{dT}$$

$$\hookrightarrow \quad P^{sat} = \exp\left[A + \frac{B}{RT}\right]$$

$$\frac{dP^{sat}}{dT} = -\frac{B \exp(A + B/RT)}{RT^2}$$

$$F'(T) = -\frac{x_5 B_5 \exp(A_5 + B_5/RT)}{RT^2} - \frac{B_7 \exp\left(A_7 + \frac{B_7}{RT}\right)}{RT^2}$$

$$+ \frac{x_5 B_7 \exp(A_7 + B_7/RT)}{RT^2}$$

With the converged T, for each x_5,

$$y_5 = \frac{x_5 P_5^{sat}(T)}{1.013}$$

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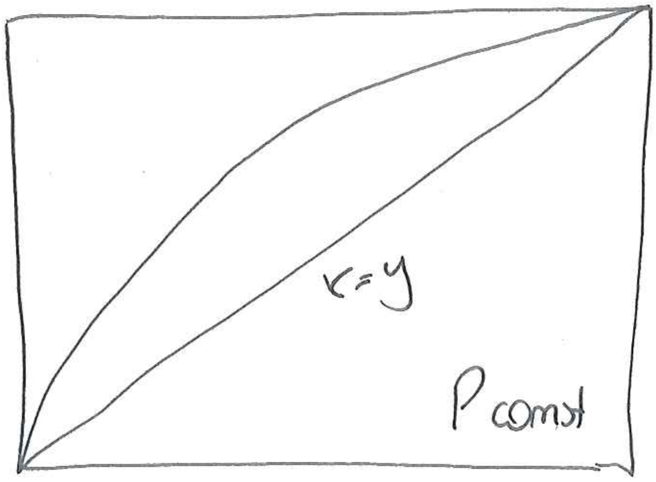
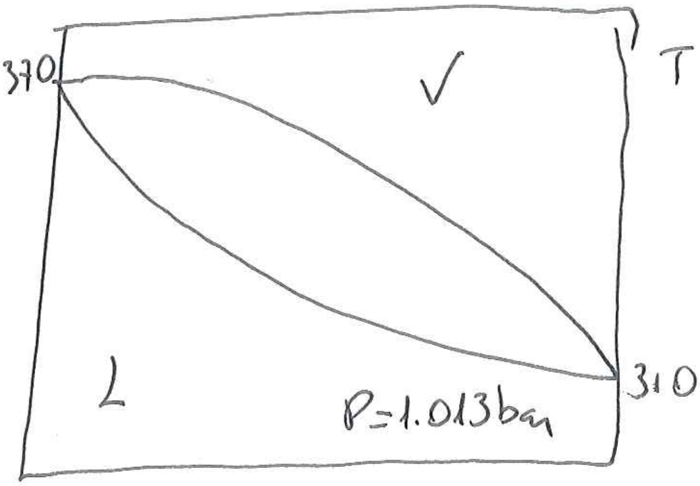
5





T (K)	x_5	y_5
370.80	0.00	0.00
357.80	0.10	0.4050
347.73	0.20	0.6249
339.73	0.30	0.7535
333.21	0.40	0.8345
327.77	0.50	0.8880
323.13	0.60	0.9257
319.12	0.70	0.9528
315.60	0.80	0.9728
312.47	0.90	0.9881
309.67	1.00	1.000

27 $\quad \frac{16}{6}$

Example 2 / Problem 2 :

nC_5 : 25% mol-%
nC_6 : 45% mol-%
nC_7 : 30% mol-%
$\Big\}$ $P = 1.013$ bar

$$\ln P_i^{sat} = A_i - B_i/RT \qquad \Big\}\ [P]: \text{bar},\ [T]: \text{K}$$

(a) DP & BP

~~From~~ Gibb's phase rule

$$\varphi = 2 + C - P = 2 + 3 - 2 = 3$$

Since $\underline{P}$ and 2 independent mole fractions of one phase have been fixed, the problem is well-posed and can be ~~posed~~ solved. Assuming the solution is ideal, and the gas phase behaves as an ideal gas (low/room pressure),

$$\left.\begin{aligned} x_i P_i^{sat} &= y_i P = P_i \\ \sum x_i P_i^{sat} &= \sum P_i = P \\ \text{with } \sum x_i = 1 \ &\&\ \sum y_i = 1 \end{aligned}\right\}$$

For the bubble point, the procedure is:

(i) choose an initial guess for bubble point temperature, T^{guess}

(ii) Calculate $y_i = \frac{x_i P_i^{sat}}{P}$

(iii) If $\sum y_i = 1 \rightarrow \underline{T^{guess} = T}$

If $\sum y_i > 1 \rightarrow T^{guess} > T$
If $\sum y_i < 1 \rightarrow T^{guess} < T$
$\Big\}$ adjust T^{guess}

Thus, for this problem

$$\sum y_i = 1 \therefore \frac{x_{C5} P_{C5}^{sat}}{P} + \frac{x_{C6} P_{C6}^{sat}}{P} + \frac{x_{C7} P_{C7}^{sat}}{P} = 1 \quad (1)$$

where $P_i^{sat} = P_i^{sat}(T)$

=> <u>Method 1</u>:

- guess T, apply to the left-hand-side of (1) until it's equal to <u>1</u>

=> <u>Method 2</u>: Newton-Raphson (iterative)

$$F = \frac{x_{C5} P_{C5}^{sat}}{P} + \frac{x_{C6} P_{C6}^{sat}}{P} + \frac{x_{C7} P_{C7}^{sat}}{P} - 1 = 0$$

From the previous problem,

$$\frac{d}{dT}\left(\frac{x_i P_i^{sat}}{P}\right) = -\frac{x_i B_i \exp(A_i + B_i/RT)}{PRT^2}$$

$$T^{i+1} = T^i - \frac{F(T^i)}{\frac{dF(T^i)}{dT}}$$

From an initial guess of 298.15 K

$T^0 = 298.15$ K

$T^1 = 364.104$ K

$T^2 = 342.584$ K

$T^3 = 335.601$ K

$T^4 = 334.943$ K

$\boxed{T^5 = 334.938 \text{ K}}$

$$\left.\begin{aligned} y_{C5} &= 0.5483 \\ y_{C6} &= 0.0883 \\ y_{C7} &= 0.3634 \end{aligned}\right\} \sum y = 1$$

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For the Dew point:

(i) choose an initial guess for dew point temperature, T^{guess}

(ii) calculate the values for $x_i = \frac{y_i P}{P_i^{sat}}$

(iii) If $\sum x_i = 1 \rightarrow T^{guess} = T$

If $\sum x_i > 1 \rightarrow T^{guess} < T$ } adjust T^{guess}

If $\sum x_i < 1 \rightarrow T^{guess} > T$

Thus for this problem

$$\sum x_i = 1 = \frac{y_{C_5} P}{P_{C_5}^{sat}} + \frac{y_{C_6} P}{P_{C_6}^{sat}} + \frac{y_{C_7} P}{P_{C_7}^{sat}} \qquad (2)$$

Where $P_i^{sat} = P_i^{sat}(T)$

$\Rightarrow$ <u>Method 1</u>:
- guess T
- apply to the rhs of (2) until it's equal to 1

$\Rightarrow$ <u>Method 2</u>: Newton-Raphson

$$F = \frac{y_{C5} P}{P_{C5}^{sat}} + \frac{y_{C6} P}{P_{C6}^{sat}} + \frac{y_{C7} P}{P_{C7}^{sat}} - 1 = 0$$

$$\frac{d}{dT}\left(\frac{y_i P}{P_i^{sat}}\right) = \frac{y_i B_i P \exp(-B_i/RT - A_i)}{RT^2}$$

$$\frac{dF}{dT} = \sum \frac{y_i B_i P \exp(-B_i/RT - A_i)}{RT^2}$$

With an initial guess of $T^0 = 300\,K$

$$T^{i+1} = T^i - F/dF/dT$$

$T^0 = 300\,K$

$T^1 = 319.1960\,K$

$T^2 = 336.3976\,K$

$T^3 = 347.2196\,K$

$T^4 = 350.3771\,K$

$T^5 = 350.5849\,K$

$T^6 = 350.5857\,K$

$\downarrow$

$x_{C5} = 0.0742$

$x_{C6} = 0.3463$

$x_{C7} = 0.5795$

(b) Now estimating the dew & bubble points at 73°C

- For the bubble point (mixture follow Raoult's law)

$$P(\text{bubble point}) = \sum x_i P_i^{sat}$$

$$= x_{C5} P_{C5}^{sat} + x_{C6} P_{C6}^{sat} + x_{C7} P_{C7}^{sat}$$

$$P(bp) = 0.25 \times 3.034 + 0.45 \times 1.155 + 0.30 \times 0.449 =$$
$$= 1.413 \text{ bar}$$

The mole fraction of the vapour phase is:

$$y_i = \frac{P_i^{sat}}{P} x_i \qquad \begin{cases} y_{C5} = 0.537 \\ y_{C6} = 0.368 \\ y_{C7} = 0.095 \end{cases}$$

- For the dew point
  - Choose an initial guess for dew point pressure, P_{guess}
  - calculate $x_i = P y_i / P_i^{sat}$
  - if $\sum x_i = 1 \longrightarrow P_{guess} = P$
    $> 1 \longrightarrow P_{guess} > P$
    $< 1 \longrightarrow P_{guess} < P$

Similarly to the previous problem, we can choose Method 1 or Method 2

For Method 2,

$$F = \frac{P y_{C5}}{P_{C5}^{sat}} + \frac{P y_{C6}}{P_{C6}^{sat}} + \frac{P y_{C7}}{P_{C7}^{sat}} - 1 = 0$$

$$\frac{d}{dP}\left(\frac{P y_i}{P_i^{sat}}\right) = \frac{y_i}{P_i^{sat}} \Rightarrow P^{i+1} = P^i - \frac{F(P^i)}{\frac{dF(P^i)}{dP}}$$

With an initial guess of $P^0 = 1.013$ bar

$P^0 = 1.013$ bar

$P^1 = 0.8771$ bar

$x_{C5} = 0.0723$

$x_{C6} = 0.3418$

$x_{C7} = 0.5859$

32 Example 3
Problem 3

$$\left\{\begin{array}{l} nC_5 : 25 \text{ mol\%} \\ nC_6 : 45 \text{ mol\%} \\ nC_7 : 30 \text{ mol\%} \end{array}\right.$$

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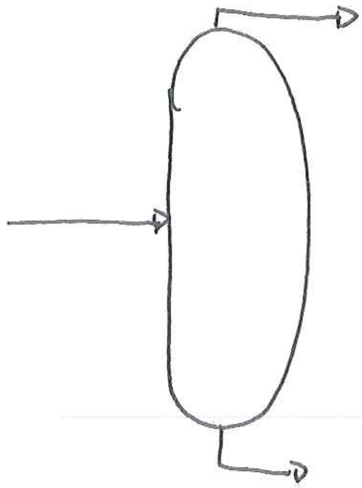

V $\quad y_{C5} \quad y_{C7} \quad y_{C6} \; \}$?

F

$z_{C5} = 0.25$

$z_{C6} = 0.45$

$z_{C7} = 0.30$

$(69°C, P)$

1.013 bar

L $\quad x_{C5} \quad x_{C7} \quad x_{C6} \; \}$?

From Antoine equation:

$$P_{C5}^{sat} = 2.721 \text{ bar} \; ; \; P_{C6}^{sat} = 1.024 \text{ bar} \; ; \; P_{C7}^{sat} = 0.389 \text{ bar}$$

Assuming ideal solution

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

and we can rewrite the relation above using K-factor:

$$\frac{y_i}{x_i} = K_i = \frac{P_i^{sat}}{P} \quad \left\{\begin{array}{l} K_{C5} = 2.6861 \\ K_{C6} = 1.0109 \\ K_{C7} = 0.3840 \end{array}\right.$$

Thus

$$\begin{cases} y_{C5} = x_{C5} K_{C5} & (1) \\ y_{C6} = x_{C6} K_{C6} & (2) \\ y_{C7} = x_{C7} K_{C7} & (3) \end{cases}$$

In addition:

$$\begin{cases} x_{C5} + x_{C6} + x_{C7} = 1 & (4) \\ y_{C5} + y_{C6} + y_{C7} = 1 & (5) \end{cases}$$

Assuming $F = 1$ $\therefore$ $F = V + L = 1$. And the mass balance of the individual components are:

$$\begin{cases} x_{C5} L + y_{C5} V = z_{C5} = 0.25 & (6) \\ x_{C6} L + y_{C6} V = z_{C6} = 0.45 & (7) \\ x_{C7} L + y_{C7} V = z_{C7} = 0.30 & (8) \\ L + V = 1 & (9) \end{cases}$$

Reducing the number of algebraic equations,

(1-3) in (5)

$$x_{C5} + x_{C6} + x_{C7} = 1 \quad (10)$$

(9&1) in (6)

$$K_{C5} x_{C5} + K_{C6} x_{C6} + K_{C7} x_{C7} = 1 \quad (11)$$

$$x_{C5}\left[L + K_{C5}(1-L)\right] = x_{C5}\left[L(1-K_{C5}) + K_{C5}\right] = 0.25 \quad (12)$$

$$x_{C6}\left[L(1-K_{C6}) + K_{C6}\right] = 0.45 \quad (13)$$

$$x_{7}\left[L(1-K_{C7}) + K_{C7}\right] = 0.30 \quad (14)$$

This is a system of 5 algebraic equations with 4 unknowns: x_{C5}, x_{C6}, x_{C7} and L.

However Eqns (12-14) are linear functionals, i.e.,

$$x_i = x_i(L)$$

and Eqns (10-11) are linearly independent equations that can be written as functions of L (by substituting x_i by Eqns 12-14).

In order to solve this system of equations, We can determine $\underline{L}$ by replacing Eqns (12-14) in Eqn. (10)

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$$\underbrace{\frac{0.25}{(1-K_{C5})L+K_{C5}}+\frac{0.45}{(1-K_{C6})L+K_{C6}}+\frac{0.30}{(1-K_{C7})L+K_{C7}}}_{\Psi}-1=0 \qquad (15)$$

It's clear that Eqn. (15) is a polynomial of order 3, i.e.,

$$\Gamma L^3+\alpha L^2+\beta L+\gamma=0 \qquad (16)$$

There are two main ~~strategies~~ strategies to solve this problem:

(A) Guess solving method

- initial guess of $\underline{L}$ (e.g., $L=0.5$)
- replace $\underline{L}$ in Eqn. (15) and calculate the residual $\underline{R}=\Psi-1$;
- If $\underline{R}$ is smaller than a pre-defined tolerance (e.g., 10^{-5}), than the guessed $\underline{L}$ is the solution, otherwise;

- make another guess of L and restart the calculation until convergence.

(B) Iterative method: we can rewrite Eqn. (15) as:

$$\frac{0.25}{AL+B} + \frac{0.45}{CL+D} + \frac{0.30}{EL+F} = 1 \qquad (17)$$

with $A = 1 - K_{C5}$; $B = K_{C5}$
$C = 1 - K_{C6}$; $D = K_{C6}$
$E = 1 - K_{C7}$; $F = K_{C7}$

In a polynomial form (Eqn. 16),

$$\Gamma L^3 + \alpha L^2 + \beta L + \gamma = 0 = \Phi$$

with:

$\Gamma = ACE$

$\alpha = (ADE + BCE + ACF) - (0.25\,CE + 0.45\,AE + 0.30\,AC)$

$\beta = (BDE + ADF + BCF - [0.25(CF+DE) + 0.45(AF+BE) +$
$\quad + 0.30(AD+BC)]$

$\gamma = BDF - (0.25\,DF + 0.45\,BF + 0.30\,BD)$

And for Newton-Raphson Method, we also need

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$$\frac{d\Phi}{dL} = 3\Gamma L^2 + 2\alpha L + \beta$$

Thus

$$L^{i+1} = L^i - \frac{\Phi(L^i)}{\left[d\Phi/dL\,(L^i)\right]}$$

For $L^0 = 0.50$

$L^1 = 0.5650$

$L^2 = 0.5746$

$L^3 = 0.5748 \rightarrow$

$$\left.\begin{aligned} x_{C_5} &= 0.1456 \\ x_{C_6} &= 0.4479 \\ x_{C_7} &= 0.4065 \end{aligned}\right\} \text{from } (12\text{-}14)$$

$\hookrightarrow \sum x = 1$

$L + V = 1 \therefore V = 0.4252$

$$\left.\begin{aligned} y_{C_5} &= K_{C_5} x_{C_5} = 0.3911 \\ y_{C_6} &= K_{C_6} x_{C_6} = 0.4528 \\ y_{C_7} &= K_{C_7} x_{C_7} = 0.1561 \end{aligned}\right\} \text{from } (1\text{-}3) \Rightarrow \sum y = 1$$

Problem 4:

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$$P_{C5}^{sat} = \exp\left(A_{C5} - \frac{B_{C5}}{T + C_{C5}}\right) = 185.6718 \text{ KPa}$$

$$P_{C7}^{sat} = 23.0264 \text{ KPa}$$

$$P = \frac{P_{C5}^{sat} + P_{C7}^{sat}}{2} = 104.3491 \text{ KPa} \cong 1.0435 \text{ bar}$$

For such low/moderate pressure we can assume that the Raoult law is valid, thus

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

$$y_{C5} P = x_{C5} P_{C5}^{sat} \quad \therefore \quad y_{C5} = \frac{x_{C5} P_{C5}^{sat}}{P}$$

x_{C5}	y_{C5}
0.10	0.1779
0.30	0.5338
0.50	0.8897

Problem 5:

$x_1 = 0.002 \therefore x_2 = 1 - x_1 = 0.998$

$y_1 = 0.950 \therefore y_2 = 1 - y_1 = 0.050$

Calculating the activity coefficient

$\ln \gamma_1 = 0.93\, x_2^2 \therefore \gamma_1 = 2.5251$

$\ln \gamma_2 = 0.93\, x_1^2 \therefore \gamma_2 = 1.0000$

The modified Raoult's law

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

$$P = \frac{x_i \gamma_i P_i^{sat}}{y_i} = \frac{x_1 \gamma_1 P_1^{sat}}{y_1} = \frac{x_2 \gamma_2 P_2^{sat}}{y_2}$$

$$\frac{P_1^{sat}}{P_2^{sat}} = \frac{x_2 \gamma_2 y_1}{x_1 \gamma_1 y_2} = \frac{0.9481}{2.5251 \times 10^{-4}} = \underbrace{3754.7028}_{\alpha}$$

$$\frac{P_1^{sat}}{P_2^{sat}} = \frac{\exp(A_1 - B_1/T)}{\exp(A_2 - B_2/T)} = \exp\left[A_1 - \frac{B_1}{T} - A_2 + \frac{B_2}{T}\right] = \alpha$$

$$\left[A_1 - B_1/T - A_2 + B_2/T\right] = \ln \alpha$$

$$(A_1 - A_2) - \frac{1}{T}(B_1 - B_2) = \ln \alpha$$

$$T = \frac{B_1 - B_2}{A_1 - A_2 - \ln \alpha} = \boxed{376.4532\ K}$$

$$P = \frac{x_1 \gamma_1 P_1^{sat}}{y_1} = \frac{0.002 \times 2.5251 \times \exp(A_1 - B_1/T)}{0950}$$

$$\boxed{P = 0.1368\ bar}$$

Problem 6:

Mole fraction of water in air → Raoult's law (liquid water is regarded as pure)

$$y_2 P = P_2^{sat} \therefore y_2 = \frac{P_2^{sat}}{P}$$

Saturation pressure of water at 25°C and 1 bar can be obtained from steam tables ∴ $P_2^{sat} = 0.03169$ bar

$$y_2 = \frac{0.03169 \text{ bar}}{1.01325 \text{ bar}} = 3.1276 \times 10^{-2} \Rightarrow y_1 = 09687$$

We can apply Henry's law to determine $\underline{\underline{x_1}}$

$$y_i P = x_i H_i$$

$$H_1 = 72950 \text{ bar}$$

$$x_1 = \frac{y_1 P}{H_1} = \frac{09687 \times 1.01325}{72950} = \underline{\underline{1.3455 \times 10^{-5}}}$$

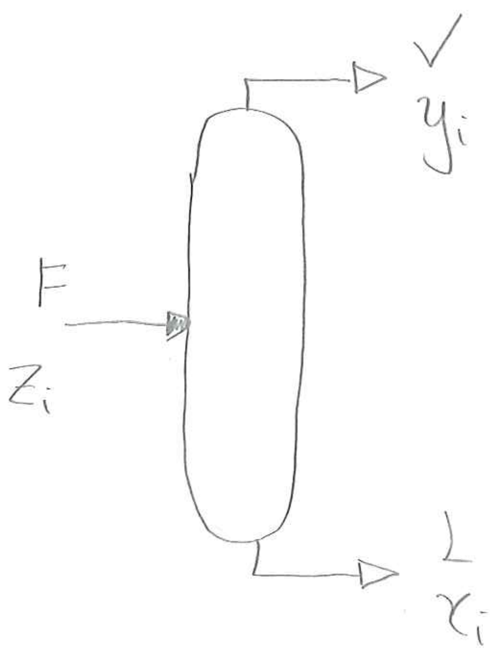
Problem 7:

Acetone (1) Methanol (2) $\left\{ \begin{array}{l} z_1 = 0.25 \\ P = 1 \text{ bar} \end{array} \right.$ $T?$ $(x_1 = 0.175)$

As γ_i is given, we can not consider the solution as ideal, therefore the modified Raoult's law can be used

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

$$y_1 = \frac{x_1 \gamma_1 P_1^{sat}}{P}$$



$$F z_1 = x_1 L + y_1 V$$

For $F = 1$ $\therefore$ $F = L + V = 1$

$$z_1 = x_1 L + \frac{x_1 \gamma_1 P_1^{sat}}{P} \cdot (1 - L) \qquad (1)$$

$$P = \sum P_i = y_1 P + y_2 P = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat} \quad (2)$$

Therefore, we have 2 equations and 2 unknowns

(α and T). Let's solve (2) first for T:

$$P = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat}$$

$$\Phi = P - \left[x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat} \right]$$

where $P_i^{sat} = P_i^{sat}(T) = \exp\left[A_i - \dfrac{B_i}{T + C_i} \right]$

$$\frac{d\Phi}{dT} = -\left[\frac{x_1 B_1 \gamma_1 \exp\left[A_1 - B_1/(T+C_1)\right]}{(T+C_1)^2} + \frac{x_2 B_2 \gamma_2 \exp\left[A_2 - B_2/(T-C_2)\right]}{(T+C_2)^2} \right]$$

$$T^{i+1} = T^i - \frac{\Phi(T^i)}{d\Phi/dT\,(T^i)}$$

With initial guess $T^0 = 100\,°C$

$T^0 = 100\,°C$ $\quad$ $T^4 = 59.53\,°C$

$T^1 = 75.14\,°C$

$T^2 = 62.65\,°C$

$T^3 = 59.68\,°C$

With I we can solve (1) for L

$$z_1 = x_1 L + \frac{x_1 \gamma_1 P_1^{sat}}{P}(1-L)$$

$$z_1 = \left[x_1 - \frac{x_1 \gamma_1 P_1^{sat}}{P}\right] L + \frac{x_1 \gamma_1 P_1^{sat}}{P}$$

$$L = \frac{z_1 - x_1 \gamma_1 P_1^{sat}/P}{x_1 - x_1 \gamma_1 P_1^{sat}/P} = \underline{0.4306} \therefore \underline{V = 0.5694}$$

$$y_1 = \frac{x_1 \gamma_1 P_1^{sat}}{P} = \underline{0.3067} \therefore \underline{y_2 = 0.6933}$$