Problem 26

1. 70% He, 30% CH₄
   P = 10 bar
   T = 117°C

2. 47% He, 3% CH₄
   P = 15 bar
   T = 50°C

3. 0.7% He, 90% CH₄
   P = 1 bar
   T = 27°C

Adiabatic, Q = 0

Material balances, using 1 mole of feed as a basis:

Balance on He:
0.7 = 0.47n₂ + 0.1n₃

Balance on CH₄:
0.3 = 0.03n₂ + 0.9n₃

n₂ = 0.69 moles
n₃ = 0.3 moles

So we have:

p = 15 bar
T = 50°C

0.03% He
0.0207 CH₄

x₉e = 0.97
x₈CH₄ = 0.03

p = 1 bar
T = 27°C

0.031% He
0.27% CH₄

x₉e = 0.1
x₈CH₄ = 0.9
Problem 27

a) At constant $T$ and $P$

\[ \sum_i x_i \lambda_i \bar{M}_i = 0 \]

see if \[ x_1 \lambda_1 \frac{d \bar{H}_1}{dx_1} + x_2 \lambda_2 \frac{d \bar{H}_2}{dx_2} = 0 \]
or \[ x_1 \lambda_1 \frac{d \bar{H}_1}{dx_1} + x_2 \lambda_2 \frac{d \bar{H}_2}{dx_2} = 0 \]

\[ \bar{H}_1 = x_1 (a_1 + b_1 x_1) \]
\[ \frac{d \bar{H}_1}{dx_1} = (a_1 + b_1 x_1) + b_1 \lambda_1 = a_1 + 2b_1 x_1 \]

\[ \bar{H}_2 = x_2 (a_2 + b_2 x_2) \]
\[ \frac{d \bar{H}_2}{dx_2} = -a_2 + 2b_2 (1 - x_1) = -a_2 + 2b_2 x_2 \]

\[ x_1 \lambda_1 \frac{d \bar{H}_1}{dx_1} + x_2 \lambda_2 \frac{d \bar{H}_2}{dx_2} = x_1 (a_1 + 2b_1 x_1) + x_2 (-a_2 + 2b_2 x_2) \]
\[ = x_1 a_1 + 2b_1 x_1^2 - a_2 x_2 - 2b_2 x_2^2 \]
\[ = -a_2 + 2b_2 x_2 + (a_1 + a_2 + 4b_1) x_1 + 2(b_1 - b_2) x_1^2 \]

which in general $\neq 0$, \[ \bar{H}_i \neq x_i \lambda_i (a_i + b_i x_i) \]

unless \[ b_1 = b_2 = b \]

and \[ a_1 = a_2 = -2b \]

for this special case \[ \bar{H}_i = x_i \lambda_i (a_i + b_i x_i) \]
As \( S_i^y (T, P) = S_i^y (T, P_0) \)
we therefore have \( S^y = \sum_i y_i S^y_i - R \sum_i y_i \ln y_i \) \hspace{1cm} (eqn. 11.25)

\[ S_1 = 0.7 S_1^{\text{He}} + 0.3 S_1^{\text{CH}_4} - R \left( 0.7 \ln 0.7 + 0.3 \ln 0.3 \right) \]
\[ S_2 = 0.97 S_2^{\text{He}} + 0.03 S_2^{\text{CH}_4} - R \left( 0.97 \ln 0.97 + 0.03 \ln 0.03 \right) \]
\[ S_3 = 0.1 S_3^{\text{He}} + 0.9 S_3^{\text{CH}_4} - R \left( 0.1 \ln 0.1 + 0.9 \ln 0.9 \right) \]

\[ \Delta S_{\text{total}} = \left( 0.69 S_2 + 0.31 S_3 \right) - S_1 \]
\[ = 0.6693 (S_2^{\text{He}} - S_1^{\text{He}}) + 0.031 (S_3^{\text{He}} - S_1^{\text{He}}) + 0.0207 (S_2^{\text{CH}_4} - S_1^{\text{CH}_4}) \]
\[ + 0.279 (S_3^{\text{CH}_4} - S_1^{\text{CH}_4}) - 3.47 \]

* Note here that we split 0.7 \( S_1^{\text{He}} \) into 0.6693 \( S_2^{\text{He}} \) + 0.031 \( S_1^{\text{He}} \) for convenience.
For ideal gas \( \Delta S = \int \frac{C_p^y dT}{T} - R \ln \frac{P}{P_0} \)

if \( C_p^y \) is a constant \( \Rightarrow \Delta S = C_p^y \ln \frac{T}{T_0} - R \ln \frac{P}{P_0} \)

\[ \Delta S^{\text{hmr}} = 0.6693 \left( \frac{5}{2} R \ln \frac{323}{390} - R \ln \frac{15}{10} \right) + 0.031 \left( \frac{5}{2} R \ln \frac{300}{390} - R \ln \frac{15}{10} \right) \]
\[ + 0.0207 \left( \frac{4}{2} R \ln \frac{323}{390} - R \ln \frac{15}{10} \right) + 0.279 \left( \frac{4}{2} R \ln \frac{300}{390} - R \ln \frac{1}{10} \right) - 3.47 \]

\[ \Delta S = -5.535 \text{ J/K} \]

as work is produced in the process, \( \Delta S > 0 \) is to be expected

Violin of the 2nd law
b) \( H = x_1 (a_1 + b_1 x_1) + x_2 (a_2 + b_2 x_2) \)

\[ = x_1 (a_1 + b_1 x_1) + (1 - x_1) [a_2 + b_2 (1 - x_1)] \]

\[ = x_1 a_1 + b_1 x_1^2 + a_2 + b_2 - b_2 x_1 - x_1 a_2 - x_1 b_2 + b_2 x_1^2 \]

\[ = a_2 + b_2 + (a_1 - a_2 - 2b_2) x_1 + (b_1 + b_2) x_1^2 \]

\[ \frac{dH}{dx_1} = (a_1 - a_2 - 2b_2) + 2(b_1 + b_2) x_1 \]

\[ \bar{H}_1 = H + x_2 \frac{dH}{dx_1} \]

\[ = a_2 + b_2 + (a_1 - a_2 - 2b_2) x_1 + (b_1 + b_2) x_1^2 + (a_1 - a_2 - 2b_2) \]

\[ + 2 (b_1 + b_2) x_1 - (a_1 - a_2 - 2b_2) x_1 - 2 (b_1 + b_2) x_1^2 \]

\[ = (a_1 - b_2) + 2 (b_1 + b_2) x_1 - (b_1 + b_2) x_1^2 \]

\[ \bar{H}_2 = H - x_1 \frac{dM}{dx_1} \]

\[ = a_2 + b_2 + (a_1 - a_2 - 2b_2) x_1 + (b_1 + b_2) x_1^2 \]

\[ - (a_1 - a_2 - 2b_2) x_1 - 2 (b_1 + b_2) x_1^2 \]

\[ = (a_2 + b_2) - (b_1 + b_2) x_1^2 \]
For a mixture of n-octanol (1) and n-decane (2):

\[ H = x_1x_2(A + B(x_1 - x_2)) \text{ J/mol} \]

where \( A = -12,974 + 51.505 T \) and \( B = 8782.8 - 34.129 T \) with \( T \) in K.

a) Wanted: \( H_1, H_2, \overline{H}_1, \) and \( \overline{H}_2. \)

Pure n-octanol enthalpy \( (x_1 = 1) \),

\[ H_1 = H\big|_{x_1=1} = 1 \cdot 0 \cdot (A + B(1-0)) = 0 \]

Pure n-decane enthalpy \( (x_2 = 1) \),

\[ H_2 = H\big|_{x_1=0} = 0 \cdot 1 \cdot (A + B(0-1)) = 0 \] (ans)

We can use the following formulae for binary system:

\[ \overline{H}_1 = H + x_2 \frac{dH}{dx_1} \quad \text{(eq. 1)} \]

\[ \overline{H}_2 = H - x_1 \frac{dH}{dx_1} \quad \text{(eq. 2)} \]

Let us calculate the yet unknown \( H \) and \( \frac{dH}{dx_1} \) for \( x_1 = 0.5 \) and \( T = 300K \)

At 300 K,

\[ A = -12,974 + 51.505 (300) = 2477.5 \]
\[ B = 8782.8 - 34.129 (300) = -1455.9 \]

Writing \( H \) and \( \frac{dH}{dx_1} \) in terms of \( x_1 \):

\[ H = (x_1 - x_1^2)[A + B(2x_1 - 1)] \text{ J/mol} \]

\[ \frac{dH}{dx_1} = (1 - 2x_1)[A + B(2x_1 - 1)] + (x_1 - x_1^2)(2B) \text{ J/mol} \] (eq.3)

Differentiating this with \( x_1 \) also gives us:

\[ \overline{H}_1 = H + x_2 \frac{dH}{dx_1} \]

At \( x_1 = 0.5 \) and \( T = 300K \),

\[ H = (0.5 - 0.5^2)[2477.5 - 1455.9(2 \cdot 0.5 - 1)] \text{ J/mol} = 619.38 \text{ J/mol} \]

\[ \frac{dH}{dx_1} = (1 - 2 \cdot 0.5)[A + B(2 \cdot 0.5 - 1)] + (0.5 - 0.5^2)(2 \cdot (-1455.9)) = -727.95 \text{ J/mol} \]

Plugging in these values into eq.1 and eq.2, we get:

\[ \overline{H}_1 = H + x_2 \frac{dH}{dx_1} = 619.38 + 0.5 (-727.95) \text{ J/mol} = 255.4 \text{ J/mol} \] (ans)

\[ \overline{H}_2 = H - x_1 \frac{dH}{dx_1} = 619.38 - 0.5 (-727.95) \text{ J/mol} = 983.35 \text{ J/mol} \]

b) Wanted: \( C_p_1, C_p_2, \overline{C}_p_1, \) and \( \overline{C}_p_2. \)

\[ C_p = \left( \frac{\partial H}{\partial T} \right)_{P,n_i} \]

So we can simply take the derivative with \( T \) of equations 3 and 4 above:

\[ C_p = (x_1 - x_1^2)[A' + B'(2x_1 - 1)] \text{ J/mol K} \] (eq.5)

\[ \frac{dC_p}{dx_1} = (1 - 2x_1)[A' + B'(2x_1 - 1)] + (x_1 - x_1^2)(2B') \text{ J/mol K} \] (eq.6)

where \( A' = \frac{dA}{dT} = 51.505 \) and \( B' = \frac{dB}{dT} = -34.129 \).
First, calculating the pure \( C_P \)'s using eq. 5:

Pure n-octanol (\( x_1 = 1 \)), \( C_{P_1} = C_{P|x_1=1} = 1 \cdot 0 \cdot (A'+B'(1-0)) = 0 \)  

Pure n-decane (\( x_2 = 1 \)), \( C_{P_2} = C_{P|x_1=0} = 0 \cdot 1 \cdot (A'+B'(0-1)) = 0 \). (ans)

At \( x_1 = x_2 = 0.5 \) and \( T = 300 \text{K} \), using eq.5 and eq.6:

\[
\frac{dC_P}{dx_1} = (1 - 2 \cdot 0.5)[A' + B'(2 \cdot 0.5 - 1)] + (0.5 - 0.5^2)(2 \cdot (-34.129)) = -17.065 \text{J/mol K}
\]

Since \( C_P \) is also a molar property, we can use expression similar to eq.1 and eq.2 (replacing \( H \) with \( C_P \)):

\[
\bar{C}_{P_1} = C_{P} + x_2 \frac{dC_P}{dx_1} = 12.876 + 0.5 \cdot (-17.065) \text{J/mol K} = 4.344 \text{J/mol K}
\]

\[
\bar{C}_{P_2} = C_{P} - x_1 \frac{dC_P}{dx_1} = 12.876 - 0.5 \cdot (-17.065) \text{J/mol K} = 21.408 \text{J/mol K}
\]

c) Drawing the process (taking 2 mol/s of stream A as a basis)

\[
\dot{m}_A = 2 \text{ mol/s}
\]

\[
\dot{m}_B = 1 \text{ mol/s}
\]

\[x_{1,A} = 0.2\]

\[x_{1,B} = 0.9\]

Overall material balance: \( \dot{m}_C = \dot{m}_A + \dot{m}_B = (2 + 1) \text{ mol/s} = 3 \text{ mol/s} \)

Species 1 balance:

\[
x_{1,C} = \frac{\dot{m}_A x_{1,A} + \dot{m}_B x_{1,B}}{\dot{m}_C} = \frac{(2 \text{ mol/s})(0.2) + (1 \text{ mol/s})(0.9)}{3 \text{ mol/s}} = 0.433
\]

Energy balance:

\[
\Delta(mH) = \dot{Q} + \dot{W}_s = \dot{Q} = \dot{m}_C H_C - (\dot{m}_A H_A + \dot{m}_B H_B) \quad \text{(eq.7)}
\]

Calculating the enthalpies of the stream (at \( T = 300 \text{ K} \) and at each \( x_1 \)), we can use the original eq’n: \( H = x_1 x_2 (A + B (x_1 - x_2)) \text{ J/mol} \). We calculated in part a), for 300 K: \( A = 2477.5 \) and \( B = -1455.9 \).

Stream A (\( x_{1,A} = 0.2 \)):

\( H_A = (0.2)(0.8)(2477.5 - 1455.9 (0.2 - 0.8)) \text{ J/mol} = 536.2 \text{ J/mol} \)

Stream B (\( x_{1,B} = 0.9 \)):

\( H_B = (0.9)(1)(2477.5 - 1455.9 (0.9 - 0.1)) \text{ J/mol} = 118.2 \text{ J/mol} \)

Stream C (\( x_{1,C} = 0.433 \)):

\( H_C = (0.433)(0.567)(2477.5 - 1455.9 (0.433 - 0.567)) \text{ J/mol} = 656.0 \text{ J/mol} \)

Plugging in values into eq.7:

\[
\dot{Q} = \dot{m}_C H_C - (\dot{m}_A H_A + \dot{m}_B H_B) = (3 \text{ mol/s})(656 \text{ J/mol}) - [(2 \text{ mol/s})(536.2 \text{ J/mol}) + (1 \text{ mol/s})(118.2 \text{ J/mol})]
\]

\( \dot{Q} = 777.8 \text{ J/s} \). This was calculated for 3 mol/s of output stream. So for every mol of output stream we have:

\[
\dot{Q} = \frac{777.8 \text{ J/s}}{3 \text{ mol/s}} = 259.3 \text{ J/mol output} \quad \text{(ans)}
\]

Since \( Q > 0 \), heat must be added into the system.
d) Plot of $H$ vs $x_1$ at $T = 300$ K below. At $x_1 = 0.5$, $H \sim 620$ J/mol.

The partial molar enthalpies can be obtained graphically by drawing a tangent line at $x_1 = 0.5$.

\[ H_2 \sim 980 \text{ J/mol} \]

\[ H_1 \sim 260 \text{ J/mol} \]

\[ H = 0 \quad \text{at} \quad x_1 = 0 \]

\[ H_2 = 0 \quad \text{at} \quad x_1 = 1 \]

\[ \frac{dH}{dx} = 3930 \text{ J/mol} \]

\[ \frac{dH}{dx} = 1020 \text{ J/mol} \]

e) To get the infinite dilution partial enthalpies, we draw tangent lines at $x_1 = 0$ and at $x_1 = 1$.

Graphical solution is easier, but we can confirm these values through calculation – not necessary in your solution – using eqns 1 to 4 (with appropriate $x_1$’s):

\[ \overline{H}_1^\infty = H_1 \text{ at } x_1 = 0 \text{ or } x_2 = 1. \]

$At \ T = 300 \ K \ and \ x_1 = 0$, using eq. 3 and eq. 4:

\[ \frac{dH}{dx_1} = 3930 \text{ J/mol} \quad \text{and} \quad H = H_2 = 0 \]

\[ \overline{H}_1^\infty = H + x_2 \frac{dH}{dx_1} = 3930 \text{ J/mol} \]

\[ \overline{H}_2^\infty = H \text{ at } x_2 = 0 \]

$At \ T = 300 \ K \ and \ x_1 = 1$,

\[ \frac{dH}{dx_1} = -1020 \text{ J/mol} \quad \text{and} \quad H = H_1 = 0 \]

\[ H_2 = \overline{H}_2^\infty = H - x_1 \frac{dH}{dx_1} = 1020 \text{ J/mol} \]