Problem Set C

Problem 9

a) To calculate theoretical flame temperature we assume
   - reaction goes to completion
   - adiabatic process \( (Q = 0) \)

reaction: \( \text{C}_3\text{H}_8 \text{y} + 5 \text{O}_2 \text{y} \rightarrow 3 \text{CO}_2 \text{y} + 4 \text{H}_2\text{O} \text{y} \)

Using a basis of 1 mole \( \text{C}_3\text{H}_8 \) + stoichiometric amount of air
the feed consists of 1 mole \( \text{C}_3\text{H}_8 \)
   5 moles \( \text{O}_2 \)

\[
\frac{7}{21} \times 5 = 18.3 \text{ moles } \text{N}_2 \quad \text{since } 21 \text{ of air is } \text{O}_2
\]

and the product will be

3 moles \( \text{CO}_2 \)
4 moles \( \text{H}_2\text{O} \)
18.3 moles \( \text{N}_2 \)

as it is a state function, the value of \( \Delta H \) does not depend on the path we choose to carry out this process.

Choose a two-step process:

1. Products
   1 bar
   \( 1 \text{ atm} \)

2. \( \text{Reactants} \)
   1 bar
298 K

\( \Delta H^{\circ} \text{at 298 K} \)
Step 1: Going from reactants at 1 bar, 298 K to products at 1 bar, 298 K

Step 2: From products at 1 bar, 298 K to products at 1 bar, TK

For step 1, this is just the heat of reaction

\[ C_3H_8 + 5O_2 \rightarrow 3O_2 + 4H_2O(g) \]

at 298 K, 1 bar

\[ \Delta H_{298, \text{rxn}} = 3 \Delta H_{f, 298, \text{O}_2} + 4 \Delta H_{f, 298, \text{H}_2\text{O}(g)} - \Delta H_{f, 298, \text{C}_3\text{H}_8} \]

\[ = 3 \times (-393.507) + 4 \times (-2418.8) - (-1046.80) \]

\[ = -2043119 \text{ J} \] (Data in table 4)

For step 2:

\[ \Delta H^T = \Delta H_{\text{product, 1 bar, TK}} - \Delta H_{\text{product, 1 bar, 298K}} \]

\[ = \int_{298}^{T} C_p^0 \, dT \]

\[ C_p^0, \text{ product} = 3 \left( C_p^0, \text{O}_2 + 4 \left( C_p^0, \text{H}_2\text{O}(g) + 18.8 \left( C_p^0, \text{N}_2 \right) \right) \right) \]

assuming the gas is ideal
From Table C1 in SUNA, we have data of the form

\[
\frac{C_p}{R} = A + BT + CT^2 + DT^{-2}
\]

\[
\frac{C_p^0_{\text{product}}}{R} = 3 \times 5.457 + 4 \times 3.470 + 12.8 \times 3.280
\]

\[
+ (3 \times 1.045 \times 10^{-2} + 4 \times 1.450 \times 10^{-3} + 18.8 \times 0.573 \times 10^{-3}) T
\]

\[
+ (3 \times -0.157 \times 10^{-5} + 4 \times 0.121 \times 10^{-5} + 18.8 \times 0.04 \times 10^{-5}) T^{-2}
\]

\[
= 91.915 + 0.02 T - 2.235 \times 10^5 T^{-2}
\]

\[
\Delta H_p^0 = R \int_{298}^{T} \left( 91.915 + 0.02 T - 2.235 \times 10^5 T^{-2} \right) dT
\]

\[
= R \left[ 91.915 T + 0.01 T^2 + 2.235 \times 10^5 T^{-1} \right]_{298}^{T}
\]

\[
= R \left( 91.915 T + 0.01 T^2 + 2.235 \times 10^5 T^{-1} - 290.29 \right)
\]

\[
\Delta H = \Delta H_0 + \Delta H_2
\]

\[
= R \left( 91.915 T + 0.01 T^2 + 2.235 \times 10^5 T^{-1} \right) - 22844.66
\]

For a constant pressure process,

\[
Q = n \Delta H
\]

Since \( Q = 0 \):

\[
\Delta H = 0
\]
we can solve this equation iteratively by guessing the value of $T$, and put it in the right hand side of the equation above. The answer can be used as a better estimate for the next iteration. Eventually you will get

$$T = \frac{2072.418 - 0.01T^2 - 2.235 \times 10^5 T}{91.915}$$

$$T = 2375 \text{ K}$$

b) If we used 10% excess air, then the conditions become

**Inlet**

- 1 mole $\text{C}_3\text{H}_8$
- 5.5 moles $\text{O}_2$
- 20.7 moles $\text{N}_2$

**Outlet**

- 3 moles $\text{CO}_2$
- 4 moles $\text{H}_2\text{O(g)}$
- 0.5 moles $\text{O}_2 \leftarrow$ excess $\text{O}_2$
- 20.7 moles $\text{N}_2 \not \rightarrow$ not reacted

In this case, $\Delta H$ for step 1 is the same

ie. $\Delta H_0 = -2043119 \text{ J}$

$\Delta H$ for step 2 will have the same numerical value, but the expression will have to be modified for new outlet concentrations.
Here we have

\[\Delta H^\circ = \int_0^{298} R \left[ 100 + 0.0215T - 2.2725 \times 10^5 T^{-2} \right] dT\]

\[= R \left[ 100 T + 0.01075 T^2 + 2.2725 \times 10^5 T^{-1} \right]_{298}^T\]

\[= R \left( 100 T + 0.01075 T^2 + 2.2725 \times 10^5 T^{-1} - 315.17 \right)\]

as \[\Delta H = 0\]

\[R \left( 100 T + 0.01075 T^2 + 2.2725 \times 10^5 T^{-1} \right) - 2305.15 = 0\]

\[T = 2235 \text{ K}\]
C) For a 10% deficiency of air

Inlet

- 1 mole $C_3H_8$
- 4.5 moles $O_2$
- 16.9 moles $N_2$

Outlet

- 2.7 moles $CO_2$
- 3.6 moles $H_2O$\(g\)
- 16.9 moles $N_2$
- 0.1 moles $C_3H_8 \leftarrow$ excess unburnt $C_3H_8$

in this case the reaction would only reach 90% conversion of propane,

in which case

\[ \Delta H^0_{\text{rxn, 90\% conversion}} = 0.90 \times -204.2n99 = -18.38807\text{J} \]

\[ \Delta H^0_{\text{rxn, 100\% conversion}} \]

\[ C_{p, \text{product}} = 2.7 \times C_{p, c_2} + 3.6 \times C_{p, H_2O} + 16.9 \times C_{p, N_2} + 0.1 \times C_{p, C_3H_8} \]

\[ C_{p, \text{product}} = \frac{8278 + 0.0209T - 8.824 \times 10^{-7}T^2 - 201230}{R} \]

\[ \Delta H^0_p = R \int_{298}^{T} \left( 82.78T + 0.0209T - 8.824 \times 10^{-7}T^2 - 201230T^{-1} \right) dT \]

\[ = R \left[ 82.78T + 0.01045T^2 - 2.941 \times 10^{-7}T^3 + 201230T^{-1} \right]_{298}^{T} \]

\[ = R \left( 82.78T + 0.01045T^2 - 2.941 \times 10^{-7}T^3 + 201230T^{-1} - 26214 \right) \]
as \( \Delta H = \Delta H^0 + \Delta H^\circ = 0 \)

\[ R(32.73T + 0.01045T^2 - 2.941 \times 10^{-9}T^3 + 201230T^{-1}) - 205.7166 = 0 \]

\( T = 2340 \text{ K} \)

d) For a stoichiometric feed with 95% conversion we have

Inlet

- 1 mole \( C_3H_8 \)
- 5 moles \( O_2 \)
- 18.8 moles \( N_2 \)

Outlet

- 2.85 moles \( CO_2 \)
- 3.8 moles \( H_2O \) (g)
- 18.8 moles \( N_2 \)
- 0.05 moles \( C_3H_8 \)
- 0.25 moles \( O_2 \)

For a 95% conversion, \( \Delta H_{\text{mole}} = \Delta H^0 = -19409.63 \text{ J} \)

\[
\frac{C_p^0}{R} = 91.37 + 0.0212T - 4.412 \times 10^{-7}T^2 - 214240T^{-2}
\]

\[
\Delta H^\circ = \Delta H^\circ = R \int_{298}^{T} \left[ 91.37 + 0.0212T - 4.412 \times 10^{-7}T^2 - 214240T^{-2} \right] dT
\]

\[
= R \left[ 91.37T + 0.0106T^2 - 1.471 \times 10^{-9}T^3 + 214240T^{-1} \right]_{298}^{T}
\]

\[
= R \left( 91.37T + 0.0106T^2 - 1.471 \times 10^{-9}T^3 + 214240T^{-1} - 23885 \right)
\]
with $A_1 = 0$

we have $R(11.37 T + 0.0106 T^2 - 1.471 \times 10^{-3} T^3 + 214240 T^{-1}) - 218110 = 0$

$T = 2285 \text{ K}$

2) - heat lost to surroundings
- some of the coefficients for heat capacities calculations only valid up to 1500 K (see Table C1)
- the gases are not ideal
Problem 10

Molar volume of steam at 63 bar and 300°C

a) Ideal gas EOS

\[ PV = RT \]
\[ V = \frac{RT}{P} \]
\[ = \frac{8.314 \times 573}{63 \times 10^5} \]
\[ V = 7 \times 10^{-4} \text{ m}^3/\text{mol} \]

b) van der Waals

\[ p = \frac{RT}{V-b} - \frac{a}{V^2} \]

\[ a = 0.421875 R^2 T_c^2 \]
\[ \text{For water } \ T_c = 647.1 \text{ K} \]
\[ \text{P}_c = 220.55 \text{ bar} \]
\[ \therefore a = \frac{0.421875 \times 8.314^2 \times 647.1^2}{220.55 \times 10^5} = 0.554 \]
\[ b = 0.125 \frac{RT_c}{P_c} \]
\[ b = \frac{0.125 \times 8.314 \times 647.1}{220.55 \times 10^5} = 3.05 \times 10^{-5} \]

Rearrange the van der Waals eqn.

\[ P(V-b)V^2 = RTV^2 - a(V-b) \]
\[ PV^3 - (bP + RT)V^2 + aV - ab = 0 \]
\( V^3 - \frac{(b + RT)}{P} V^2 + \frac{a V}{P} - \frac{ab}{P} = 0 \)

Substitute for \( a, b, R, T, \) and \( P \)

\( V^3 - 7.31 \times 10^{-4} V^2 + 8.14 \times 10^{-3} V - 2.43 \times 10^{-12} = 0 \)

\[
V = 6.03 \times 10^{-4} \text{ m}^3/\text{mol}
\]

The other two solutions are complex numbers. Not relevant

C) Redlich-Kwong EOS

\[
P = \frac{RT}{V-b} - \frac{a}{T^{1/2} V(V+b)}
\]

\[
a = 0.42348 \frac{R^2 T_c^{2.5}}{P_c}
\]

\[
b = 0.08164 \frac{P_c T_c}{P_c}
\]

\[
a = 14.27
\]

\[
b = 2.11 \times 10^{-5}
\]

Rearrange the eqn.

\[
P (V-b) T^{1/2} V (V+b) = RT^{3/2} V (V+b) - a (V-b)
\]

\[
P T^{1/2} (V^3 - b^2 V) = RT^{3/2} (V^3 + bV) - a (V-b)
\]

\[
P T^{1/2} V^3 = RT^{3/2} V^2 + (a - RT^{1/2} b^2 - RT^{3/2} b) V - ab = 0
\]

\[
V^3 - \frac{RT}{P} V^2 + \left( \frac{a}{P T^{1/2}} - b^2 - \frac{RT b}{P} \right) V - \frac{ab}{P T^{1/2}} = 0
\]
\[ V^3 = 7 \times 10^{-4} V^2 + 7.24 \times 10^{-8} V - 1.85 \times 10^{-12} = 0 \]

\[ V = 5.81 \times 10^{-4} \text{ m}^3/\text{mol} \]

\[ T_c = 647.1 \text{ K} \quad P_c = 220.55 \text{ bar} \]

\[ T_r = \frac{T_c}{T_r} = \frac{573}{647.1} = 0.885 \quad P_r = \frac{P}{P_c} = \frac{68}{220.55} = 0.308 \]

From interpolations of table E1, and E2, or from chart

\[ Z^0 = 0.717 \quad Z^1 = -0.071 \]

With \( W = 0.345 \) for \( H_2O \) (Table B1)

\[ Z = Z^0 + W Z^1 = 0.717 + 0.345 \times (-0.071) = 0.693 \]

\[ V = \frac{ZRT}{P} = \frac{0.693 \times 8.314 \times 573}{68 \times 10^5} \]

\[ V = 4.35 \times 10^{-4} \text{ m}^3/\text{mol} \]

\( V = \frac{30.652 \text{ cm}^3/\text{g}}{\frac{18 \text{ g} \ H_2O}{1 \text{ mol \ H}_2\text{O}}} \times \frac{1 \text{ m}^3}{10^4 \text{ cm}^3} \]

\[ V = 5.52 \times 10^{-4} \text{ m}^3/\text{mol} \]
11.

a) $\text{SO}_2(g) + \text{O}_2(g) \rightarrow \text{SO}_3(g)$

Writing what we know plus data from Appendix C:

<table>
<thead>
<tr>
<th>Stoich. coef. ν</th>
<th>$\text{SO}_2(g)$</th>
<th>$\text{O}_2(g)$</th>
<th>$\text{SO}_3(g)$</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H^0_{298}$ (J/mol)</td>
<td>-296830</td>
<td>0</td>
<td>-395720</td>
<td>-98890</td>
</tr>
<tr>
<td>A</td>
<td>5.699</td>
<td>3.639</td>
<td>8.06</td>
<td>-1.278</td>
</tr>
<tr>
<td>B</td>
<td>0.801E-03</td>
<td>0.506E-03</td>
<td>1.056E-03</td>
<td>-0.251E-03</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>D</td>
<td>-1.015E+05</td>
<td>-0.227E+05</td>
<td>-2.028E+05</td>
<td>-0.786E+05</td>
</tr>
</tbody>
</table>

where $\frac{C_p}{R} = A + BT + CT^2 + DT^{-2}$

Here $\Delta X = \Sigma \nu_i X_i$

For example:

$\Delta A = A_{\text{SO}_3} - A_{\text{SO}_2} - A_{\text{O}_2}$

$\Delta H_{\text{rxn},298} = \Delta H_{fSO_3} - [\Delta H_{fSO_2} + \Delta H_{fO_2}] = (-395720) - (-296830) = \mathbf{-98,890 \text{ J/mol}}$ (at 298K)

$\Delta H_{\text{rxn},750} = \Delta H_{\text{rxn},298} + \Sigma \int \nu_i C_p \, dT$

$= \Delta H_{\text{rxn},298} + \Sigma \nu_i \int R(A_i + B_i T + C_i T^2 + D_i T^{-2}) \, dT$

$= \Delta H_{\text{rxn},298} + \Sigma \nu_i [R[A_i (T_2 - T_1) + 1/2 B_i (T_2^2 - T_1^2) + 1/3 C_i (T_2^3 - T_1^3) - D_i (T_2^{-1} - T_1^{-1})]]$

$T_2 = 750 \text{ K} \quad T_1 = 298 \text{ K} \quad R = 8.314 \text{ J/mol K}$

$\Delta H_{\text{rxn},750} = -98890 \text{ J/mol} + 8.314 \text{ J/mol K} \cdot [-1.278 (750 - 298) + 1/2 (-0.251 \times 10^{-3}) (750^2 - 298^2) + 1/3 (0) (750^3 - 298^3) - (-0.786 \times 10^2) (750^{-1} - 298^{-1})]$ K

$\Delta H_{\text{rxn},750} = \mathbf{-105,508 \text{ J/mol}}$ (at 750 K)

b) $\text{CaO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca(OH)}_2(s)$

<table>
<thead>
<tr>
<th>Stoich. coef. ν</th>
<th>$\text{CaO}(s)$</th>
<th>$\text{H}_2\text{O}(l)$</th>
<th>$\text{Ca(OH)}_2(s)$</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H^0_{298}$ (J/mol)</td>
<td>-635090</td>
<td>-285830</td>
<td>-986090</td>
<td>-65170</td>
</tr>
</tbody>
</table>

$\Delta H_{\text{rxn},298} = \Delta H_{f\text{Ca(OH)}_2} - [\Delta H_{f\text{CaO}} + \Delta H_{f\text{H}_2\text{O}(l)}] = \mathbf{-65,170 \text{ J/mol}}$ (at 298K)
Now looking at the reaction at 750 K (where the H₂O is now gas instead of liquid):

\[
\text{CaO(s)} + \text{H₂O(g)} \rightarrow \text{Ca(OH)₂(s)}
\]

<table>
<thead>
<tr>
<th>Stoich. coef. ν</th>
<th>CaO(s)</th>
<th>H₂O(g)</th>
<th>Ca(OH)₂(s)</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>(\Delta H^\circ_{298} (\text{J/mol}))</td>
<td>-635090</td>
<td>-241818</td>
<td>-986090</td>
<td>-109182</td>
</tr>
<tr>
<td>B</td>
<td>6.104</td>
<td>3.47</td>
<td>9.597</td>
<td>0.023</td>
</tr>
<tr>
<td>C</td>
<td>0.443E-03</td>
<td>1.450E-03</td>
<td>5.435E-03</td>
<td>3.542E-03</td>
</tr>
<tr>
<td>(\Delta H_{\text{rxn,298}} = \Delta H_{\text{f Ca(OH)₂}} - [\Delta H_{\text{f CaO}} + \Delta H_{\text{f H₂O(g)}}])</td>
<td>-109,182 J/mol (at 298K)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Following the same method of calculation as in part a):

\[
\Delta H_{\text{rxn,750}} = \Delta H_{\text{rxn,298}} + \sum v_i C_p i dT = \Delta H_{\text{rxn,298}} + R\left[\Delta A (T_2 - T_1) + \frac{1}{2} \Delta B (T_2^2 - T_1^2) + \frac{1}{3} \Delta C (T_2^3 - T_1^3) - \Delta D (T_2^{-1} - T_1^{-1})\right]
\]

\[
\Delta H_{\text{rxn,750}} = -109182 \text{ J/mol} + 8.314 \text{ J/mol K} \left[0.023 (750-298) + \frac{1}{2} (3.542 \times 10^{-3}) (750^2-298^2) + \frac{1}{3} (0) (750^3-298^3) - (0.926 \times 10^{5}) (750^{-1} - 298^{-1})\right] \text{ K}
\]

\[
\Delta H_{\text{rxn,750}} = -100,563 \text{ J/mol} (\text{at 750 K})
\]

c) The % change going between 298 K and 750 K for the first reaction is

\[
\left(\frac{-105,508 \text{ J/mol} - 98,990 \text{ J/mol}}{98,990 \text{ J/mol}}\right) = 8.4\%
\]

The % change going between 298 K and 750 K for the second reaction is

\[
\left(\frac{-100,563 \text{ J/mol} - 65,170 \text{ J/mol}}{65,170 \text{ J/mol}}\right) = 54.3\%
\]

The change in the second reaction is larger than the first one because when we go to 750K (still at 1 atm), the water is in the vapor phase. Much energy is required to vaporize the water.
12. General picture of the process: \( n_1 \) moles of methane inside a 0.1 m\(^3\) tank is initially at 25\(^\circ\)C and 1,500 kPa. Some gas (\( n_3 \) moles) flows into a gas holder whose pressure is constant at 115 kPa. The tank pressure now is 750 kPa. The volume has remained at 0.1 m\(^3\), the temperature is at \( T_2 \) and the number of moles left is \( n_2 \). We are given: \( \gamma = \frac{C_p}{C_v} = 1.31 \).

a) Temperature of tank remains constant \( \Rightarrow T_2 = T_1 \).

From ideal gas we know that: \( P_1 V_1^t = n_1 R T_1 \) and \( P_2 V_2^t = n_2 R T_2 \)

The initial number of moles \( n_1 = \frac{P_1 V_1^t}{R T_1} = \frac{1500 \times 10^3 \text{ Pa} \cdot 0.1 \text{ m}^3}{8.314 \text{ J/mol K} \cdot 298 \text{ K}} = 60.54 \) moles

Dividing the first equation by the second:

\[
\frac{P_1 V_1^t}{P_2 V_2^t} = \frac{n_1 R T_1}{n_2 R T_2} \quad \Rightarrow \quad \frac{P_1}{P_2} = \frac{n_1}{n_2} \quad \Rightarrow \quad n_2 = \frac{P_2}{P_1} n_1 = \frac{750 \text{ kPa}}{1500 \text{ kPa}} = \frac{30.27}{\text{ moles}}
\]

b) There is no heat transfer between parts of the system, and between system and surrounding. Let us look at the gas that remains in the tank (\( n_2 \) moles). We derived in class the expression relating \( P \) and \( T \) for adiabatic process:

\[
T_2 = T_1 \left( \frac{P_2}{P_1} \right) \frac{\gamma - 1}{\gamma} \quad \Rightarrow \quad T_2 = 298 \text{ K} \left( \frac{750 \text{ kPa}}{1500 \text{ kPa}} \right)^{\frac{1.31 - 1}{1.31}} = 252.9 \text{ K}
\]

Then from ideal gas we get \( n_2 = \frac{P_2 V_2^t}{R T_2} = \frac{750 \times 10^3 \text{ Pa} \cdot 0.1 \text{ m}^3}{8.314 \text{ J/mol K} \cdot 252.9 \text{ K}} = 35.67 \) moles

Initially, we have \( n_1 = 60.54 \) moles of gas in the tank (calculated in part a).

From mass balance, we can get the amount of gas in the holder, \( n_3 = n_1 - n_2 = 24.87 \) moles
To solve for $T_3$ (temperature in the gas holder), let us choose as our system all the gas $(n_1)$. Writing out the energy balance:

$$\Delta U^i = Q + W$$

$$\Delta U^i = n_2C_v(T_2 - T_1) + n_3C_v(T_3 - T_1)$$  \hspace{1cm} 1^{st} \text{ term } \Delta U^i \text{ for gas remaining in the tank } (T_1 \text{ to } T_2)$$

$$Q = 0 \text{ (adiabatic)}$$

$$W = -\int_{V_0^i}^{V_i^f} P_dV = -P_3 (V_3^f - V_0^i) = -P_3 V_3^f = -n_3RT_3$$  \hspace{1cm} \text{The work done by the system is in expanding the gas holder, which is at constant pressure } P_3. \text{ Initially the volume } V_0^i \text{ is } 0.$$

$$n_2C_v(T_2 - T_1) + n_3C_v(T_3 - T_1) = -n_3RT_3$$

$$T_3 = \frac{n_3C_vT_1 - n_2C_v(T_2 - T_1)}{n_3(C_v + R)} = \frac{n_3C_vT_1 - n_2C_v(T_2 - T_1)}{n_3C_p} = \frac{n_3T_1 - n_2(T_2 - T_1)}{n_3\gamma}$$

$$T_3 = \frac{24.87 \text{ moles}(298\text{K}) - 35.67 \text{ moles}(252.9\text{K} - 298\text{K})}{24.87 \text{ moles}(1.31)} = 187.7 \text{ K}$$

c) If we look at the expression for $T_3$ above, we see no dependence on $P$ of the gas holder. Therefore if the pressure in the gas holder is at 300 kPa instead, we will find the same temperature $187.7 \text{ K}$. 