Problem Set C

Problem 9

a) To calculate theoretical flame temperature we assume

- reaction goes to completion
- adiabatic process $(Q = 0)$

Reaction : $C_3H_{8(g)} + 5\,O_{2(g)} \longrightarrow 3CO_{2(g)} + 4\,H_2O_{(g)}$

Using a basis of 1 mole C_3H_8 + stoichiometric amount of air

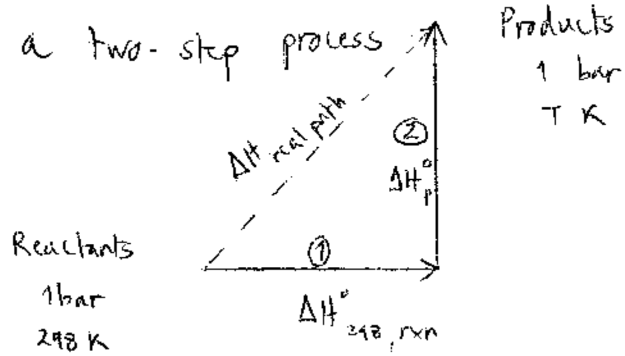
the feed consists of
1 mole C_3H_8
5 moles O_2
$\frac{79}{21} \times 5 = 18.8$ moles N_2 since 21 % air is O_2

and the product will be

3 moles CO_2
4 moles H_2O
13.8 moles N_2

As H is a state function, the value of ΔH does not depend on the path we choose to carry out this process

$\therefore$ choose a two-step process



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, T K

For step 1, this is just the heat of reaction

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O(g)$$

at 298 K, 1 bar

$$\Delta H^{\circ}_{298,rxn} = 3\,\Delta H^{\circ}_{f,298,CO_2} + 4\,\Delta H^{\circ}_{f,298,H_2O(g)} - \Delta H^{\circ}_{f,298,C_3H_8}$$

$$= 3\times(-393509) + 4\times(-241818) - (-104680)$$

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

For step 2,

$$\Delta H^{\circ}_{p} = \Delta H^{\circ}_{product,\,1bar,\,TK} - \Delta H^{\circ}_{product,\,1bar,\,298K}$$

$$= \int_{298}^{T} C_p^{\circ}\, dT$$

$$C_{p^{\circ},\,product} = 3\,C_{p^{\circ},CO_2} + 4\,C_{p^{\circ},H_2O(g)} + 18.8\,C_{p^{\circ},N_2}$$

assuming the gas is ideal

From table C1 in SUNA, we have data of the form

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

$$\therefore \frac{C_p^\circ}{R}\text{ product} = 3\times 5.457 + 4\times 3.470 + 18.8\times 3.280$$

$$+ (3\times 1.045\times10^{-3} + 4\times 1.450\times10^{-3} + 18.8\times 0.593\times10^{-3})T$$

$$+ (3\times -1.157\times10^{5} + 4\times 0.121\times10^{5} + 18.8\times 0.04\times10^{5})T^{-2}$$

$$= 91.915 + 0.02\,T - 2.235\times10^5\,T^{-2}$$

$$\therefore \Delta H_p^\circ = R\int_{298}^{T} 91.915 + 0.02\,T - 2.235\times10^5\,T^{-2}\,dT$$

$$= R\left[91.915\,T + 0.01\,T^2 + 2.235\times10^5\,T^{-1}\right]_{298}^{T}$$

$$= R\left(91.915\,T + 0.01\,T^2 + 2.235\times10^5\,T^{-1} - 29029\right)$$

$$\therefore \Delta H = \Delta H_{1} + \Delta H_{2}$$

$$= R\left(91.915\,T + 0.01\,T^2 + 2.235\times10^5\,T^{-1}\right) - 228466$$

For a constant pressure process

$$Q = n\,\Delta H$$

since $Q = 0 \quad \therefore \Delta H = 0$

$$\therefore \quad 91.915T + 0.01T^2 + 2.235\times10^5\,T^{-1} - 2072148 = 0$$

$$T = \frac{2072148 - 0.01T^2 - 2.235\times10^5\,T}{91.915}$$

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 $\boxed{T = 2375\ K}$

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

Inlet		Outlet
1 mole C_3H_8		3 moles CO_2
5.5 moles O_2	$\longrightarrow$	4 moles $H_2O_{(g)}$
20.7 moles N_2		0.5 moles O_2 ← excess O_2 not reacted
		20.7 moles N_2

in this case ΔH for step 1 is the same

ie. $\Delta H_{①} = -2043119\ J$

ΔH for step 2 will have the same numerical value, but the expression will have to be modified for new outlet concentration here we have

$$C^{o}_{p,product} = 3\, C^{o}_{p,CO_2} + 4\, C^{o}_{p,H_2O(g)} + 0.5\, C^{o}_{p,O_2} + 20.7\, C^{o}_{p,N_2}$$

$$\frac{C^{o}_{p,product}}{R} = 100 + 0.0215\,T - 2.2725 \times 10^{5}\, T^{-2}$$

$$\therefore \quad \Delta H_p^{o} = R \int_{T}^{298} 100 + 0.0215\,T - 2.2725 \times 10^{5}\, T^{-2}\, dT$$

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

$$= R\left(100\,T + 0.01075\,T^{2} + 2.2725 \times 10^{5}\, T^{-1} - 31517\right)$$

as $\Delta H = 0$

$$\therefore \quad R\left(100\,T + 0.01075\,T^{2} + 2.2725 \times 10^{5}\, T^{-1}\right) - 2305151 = 0$$

$$\therefore \quad \boxed{T = 2235\ K}$$

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 ← excess unburnt C_3H_8

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

in which case $\Delta H_{①} = 0.90 \times \underbrace{-2043119}_{\Delta H_{rxn}\ 100\%\ \text{conversion}} = -1838807\ J$

$$C^{\circ}_{p,\,product} = 2.7\, C^{\circ}_{p,\,CO_2} + 3.6\, C^{\circ}_{p,\,H_2O(g)} + 16.9\, C^{\circ}_{p,\,N_2} + 0.1\, C^{\circ}_{p,\,C_3H_8}$$

$$\frac{C^{\circ}_{p,\,product}}{R} = 82.78 + 0.0209\,T - 8.824\times10^{-7}\,T^2 - 201230$$

$$\therefore\ \Delta H^{\circ}_{P} = R\int_{298}^{T} 82.78 + 0.0209\,T - 8.824\times10^{-7}\,T^2 - 201230\,T^{-2}\,dT$$

$$= R\left[82.78\,T + 0.01045\,T^2 - 2.941\times10^{-7}\,T^3 + 201230\,T^{-1}\right]_{298}^{T}$$

$$= R\left(82.78\,T + 0.01045\,T^2 - 2.941\times10^{-7}\,T^3 + 201230\,T^{-1} - 26214\right)$$

as $\Delta H = \Delta H_{①} + \Delta H_{②} = 0$

$$\therefore \quad R(82.78\,T + 0.01045\,T^2 - 2.941\times10^{-7}\,T^3 + 201230\,T^{-1}) - 2057166 = 0$$

$$\therefore \quad \boxed{T = 2340\text{ K}}$$

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

Inlet	Outlet
1 mole C_3H_8	2.85 moles CO_2
5 moles O_2	3.8 moles $H_2O(g)$
18.8 moles N_2	18.8 moles N_2
	0.05 moles C_3H_8
	0.25 moles O_2

For a 95 % conversion $\quad \Delta H_{rxn} = \Delta H_{①} = -1940963\text{ J}$

$$\frac{C^{\circ}_{p,\,product}}{R} = 91.37 + 0.0212\,T - 4.412\times10^{-7}\,T^2 - 214240\,T^{-2}$$

$$\Delta H_{②} = \Delta H^{\circ}_{P} = R\int_{298}^{T} 91.37 + 0.0212\,T - 4.412\times10^{-7}\,T^2 - 214240\,T^{-2}\, dT$$

$$= R\left[91.37\,T + 0.0106\,T^2 - 1.471\times10^{-7}\,T^3 + 214240\,T^{-1}\right]_{298}^{T}$$

$$= R(91.37\,T + 0.0106\,T^2 - 1.471\times10^{-7}\,T^3 + 214240\,T^{-1} - 28885)$$

with $\Delta H = 0$

we have $R(41.37T + 0.0106\,T^2 - 1.471\times10^{-7}\,T^3 + 214240\,T^{-1}) - 2181110 = 0$

$\therefore \quad \boxed{T = 2285\ K}$

2) - heat lost to surroundings
- some of the coefficients for heat capacities calculations only valid up to 1500 K (see Table (1)
- the gases are not ideal

Problem 10

- Molar volume of steam at 68 bar and 300°C

a) Ideal gas EOS

$$PV = RT$$

$$V = \frac{RT}{P}$$

$$= \frac{8.314 \times 573}{68 \times 10^5}$$

$$\boxed{V = 7\times10^{-4}\ m^3/mol}$$

b) van der Waals

- $$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$a = 0.421875\, R^2 \frac{T_c^2}{P_c} \qquad b = 0.125 \frac{RT_c}{P_c}$$

For water $T_c = 647.1$ K $\quad P_c = 220.55$ bar

$$\therefore\ a = 0.421875 \times 8.314^2 \times \frac{647.1^2}{220.55\times10^5} = 0.554$$

$$b = 0.125 \times 8.314 \times \frac{647.1}{220.55\times10^5} = 3.05\times10^{-5}$$

- earrange the van der Waals eqn.

$$P(V-b)V^2 = RTV^2 - a(V-b)$$

$$PV^3 - (bP+RT)V^2 + aV - ab = 0$$

$$V^3 - \left(b + \frac{RT}{P}\right) V^2 + \frac{aV}{P} - \frac{ab}{P} = 0$$

substitute for a, b, R, T, and P

$$V^3 - 7.31\times10^{-4} V^2 + 8.14\times10^{-8} V - 2.48\times10^{-12} = 0$$

$$\boxed{V = 6.03\times10^{-4}\ m^3/mol}$$

the other two solutions are complex numbers ∴ not relevant

c) Redlich - Kwong EOS

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

$$a = 0.42748\ \frac{R^2 T_c^{2.5}}{P_c} \qquad b = 0.08664\ \frac{RT_c}{P_c}$$

$$\therefore\ a = 14.27$$

$$b = 2.11\times10^{-5}$$

rearrange the eqn.

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

$$PT^{1/2}(V^3 - b^2V) = RT^{3/2}(V^2 + bV) - a(V-b)$$

$$PT^{1/2} V^3 - RT^{3/2} V^2 + (a - PT^{1/2} b^2 - RT^{3/2} b)V - ab = 0$$

$$V^3 - \frac{RT}{P} V^2 + \left(\frac{a}{PT^{1/2}} - b^2 - \frac{RTb}{P}\right)V - \frac{ab}{PT^{1/2}} = 0$$

$$V^3 - 7\times10^{-4} V^2 + 7.24\times10^{-8} V - 1.85\times10^{-12} = 0$$

$$\boxed{V = 5.81\times10^{-4} \ m^3/mol}$$

d) Generalized compressibility correlation

$T_c = 647.1 \ K$ $\quad P_c = 220.55$ bar

$T_r = \frac{573}{647.1} = 0.885$ $\quad P_r = \frac{68}{220.55} = 0.308$

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

$Z^0 = 0.717$ $\quad Z^1 = -0.071$

with $\omega = 0.345$ for H_2O (Table B1)

$$Z = Z^0 + \omega Z^1 = 0.717 + 0.345\times(-0.071)$$
$$= 0.693$$

$$V = \frac{ZRT}{P} = \frac{0.693\times8.314\times573}{68\times10^5}$$

$$\boxed{V = 4.85\times10^{-4} \ m^3/mol}$$

e) Steam table F2

$$V = 30.652 \ cm^3/g = 30.652 \ \frac{cm^3}{g}\times\frac{18 \ g \ H_2O}{1 \ mole \ H_2O}\times\frac{1 \ m^3}{10^6 \ cm^3}$$

$$\boxed{V = 5.52\times10^{-4} \ m^3/mol}$$

11.

a) $SO_{2(g)} + O_{2(g)} \rightarrow SO_{3(g)}$

Writing what we know plus data from Appendix C:

	$SO_{2(g)}$	$O_{2(g)}$	$SO_{3(g)}$	Δ
Stoich. coef. ν	-1	-1	1	
ΔH^o_{f298} (J/mol)	-296830	0	-395720	-98890
A	5.699	3.639	8.06	-1.278
B	0.801E-03	0.506E-03	1.056E-03	-0.251E-03
C	0	0	0	0
D	-1.015E+05	-0.227E+05	-2.028E+05	-0.786E+05

where $Cp/R = A + BT + CT^2 + DT^{-2}$ T in kelvin

Here $\Delta X = \Sigma \nu_i X_i$
For example:
$\Delta A = A_{SO3} - A_{SO2} - A_{O2}$

$\Delta H_{rxn,298} = \Delta H_{f\,SO3} - [\Delta H_{f\,SO2} + \Delta H_{f\,O2}] = (-395720) - (-296830) =$ **<u>-98,890 J/mol</u>** (at 298K)

$$\begin{aligned}\Delta H_{rxn,750} &= \Delta H_{rxn,298} + \Sigma \int \nu_i Cp_i \, dT \\ &= \Delta H_{rxn,298} + \Sigma \nu_i \int R(A_i + B_iT + C_iT^2 + D_iT^{-2})\, dT \\ &= \Delta H_{rxn,298} + \Sigma \nu_i \; R[A_i (T_2-T_1) + 1/2\, B_i (T_2^2-T_1^2) + 1/3\, C_i (T_2^3-T_1^3) - D_i \; (T_2^{-1}-T_1^{-1})] \\ &= \Delta H_{rxn,298} + R[\Delta A (T_2-T_1) + 1/2\, \Delta B (T_2^2-T_1^2) + 1/3\, \Delta C (T_2^3-T_1^3) - \Delta D \; (T_2^{-1}-T_1^{-1})]\end{aligned}$$

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

$$\Delta H_{rxn,750} = -98890 \text{ J/mol} + 8.314 \text{ J/mol K} [-1.278 (750-298) + 1/2 (-0.251 \times 10^{-3}) (750^2-298^2) + 1/3 (0) (750^3-298^3) - (-0.786 \times 10^5) (750^{-1}-298^{-1})] \text{ K}$$

$\Delta H_{rxn,750} =$ **<u>-105,508 J/mol</u>** (at 750 K)

b) $CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(s)}$

	$CaO_{(s)}$	$H_2O_{(l)}$	$Ca(OH)_{2(s)}$	Δ
Stoich. coef. ν	-1	-1	1	
ΔH^o_{f298} (J/mol)	-635090	-285830	-986090	-65170

$\Delta H_{rxn,298} = \Delta H_{f\,Ca(OH)2} - [\Delta H_{f\,CaO} + \Delta H_{fH2O(l)}] =$ **<u>-65,170 J/mol</u>** (at 298K)

Now looking at the reaction at 750 K (where the H_2O is now gas instead of liquid):

$$CaO_{(s)} + H_2O_{(g)} \rightarrow Ca(OH)_{2(s)}$$

	$CaO_{(s)}$	$H_2O_{(g)}$	$Ca(OH)_{2(s)}$	Δ
Stoich. coef. ν	-1	-1	1	
ΔH^o_{f298} (J/mol)	-635090	-241818	-986090	-109182
A	6.104	3.47	9.597	0.023
B	0.443E-03	1.450E-03	5.435E-03	3.542E-03
C	0	0	0	0
D	-1.047E+05	0.121E+05	0.000E+00	0.926E+05

$\Delta H_{rxn,298} = \Delta H_{f\,Ca(OH)2} - [\Delta H_{f\,CaO} + \Delta H_{fH2O(g)}] =$ -109,182 J/mol (at 298K)

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

$$\Delta H_{rxn,750} = \Delta H_{rxn,298} + \Sigma \int \nu_i Cp_i \, dT$$
$$= \Delta H_{rxn,298} + R[\Delta A\,(T_2 - T_1) + 1/2\,\Delta B\,(T_2^2 - T_1^2) + 1/3\,\Delta C\,(T_2^3 - T_1^3) - \Delta D\,(T_2^{-1} - T_1^{-1})]$$

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

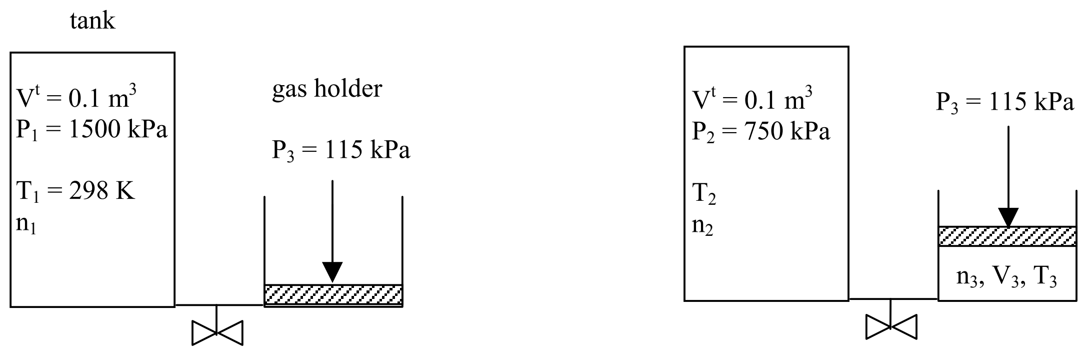
$\Delta H_{rxn,750}$ = **-100,563 J/mol** (at 750 K)

c) The % change going between 298 K and 750 K for the first reaction is
(-105,508 J/mol – 98,990 J/mol) / (98,990 J/mol) = 8.4%

The % change going between 298 K and 750 K for the second reaction is
(-100,563 J/mol – 65,170 J/mol) / (65,170 J/mol) = 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°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: $\gamma = Cp/Cv = 1.31$.

a) Temperature of tank remains constant → $T_2 = T_1$.

From ideal gas we know that: $P_1V^t_1 = n_1RT_1$ and $P_2V^t_2 = n_2RT_2$

The initial number of moles = $n_1 = \dfrac{P_1V_1^t}{RT_1} = \dfrac{1500\times 10^3\,\text{Pa}\cdot 0.1\,\text{m}^3}{8.314\ \text{J/mol K}\cdot 298\ \text{K}} = 60.54$ moles

Dividing the first equation by the second:

$$\frac{P_1V_1^t}{P_2V_2^t} = \frac{n_1RT_1}{n_2RT_2} \quad \Rightarrow \quad \frac{P_1}{P_2} = \frac{n_1}{n_2} \quad \Rightarrow n_2 = \frac{P_2}{P_1}n_1 = \frac{750\ \text{kPa}}{1500\ \text{kPa}} = \mathbf{30.27\ moles}$$

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:

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$$

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

Then from ideal gas we get $n_2 = \dfrac{P_2V_2^t}{RT_2} = \dfrac{750\times 10^3\,\text{Pa}\cdot 0.1\,\text{m}^3}{8.314\ \text{J/mol K}\cdot 252.9\ \text{K}} = 35.67$ 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:

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

$$\Delta U^t = n_2 Cv(T_2 - T_1) + n_3 Cv(T_3 - T_1)$$

1^{st} term = ΔU^t for gas remaining in the tank (T_1 to T_2)
2^{nd} term = ΔU^t for gas transferred to holder (T_1 to T_3)

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

$$W = -\int_{V_0^t}^{V_3^t} P_3 dV^t = -P_3 (V_3^t - V_0^t) = -P_3 V_3^t = -n_3 R T_3$$

The work done by the system is in expanding the gas holder, which is at constant pressure P_3. Initially the volume V_0^t is 0.

$$n_2 Cv(T_2 - T_1) + n_3 Cv(T_3 - T_1) = -n_3 R T_3$$

$$T_3 = \frac{n_3 Cv T_1 - n_2 Cv(T_2 - T_1)}{n_3 (Cv + R)} = \frac{n_3 Cv T_1 - n_2 Cv(T_2 - T_1)}{n_3 C_p} = \frac{n_3 T_1 - n_2 (T_2 - T_1)}{n_3 \gamma}$$

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

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 K.**