University of California, Irvine
Department of Mechanical and Aerospace Engineering

MAE 112 - Homework 2
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1. Calculate theoretical (ideal) flame temperature for methane in stoichiometric ratio with enriched air (50% O_2, 50% N_2 by volume). Pressure is constant at 15 atm and the initial temperature is 298 K.

Solution:
We have a stoichiometric reaction between enriched air and methane (CH_4). First, we need to balance the chemical reaction so we know the mole numbers of each species. The balanced stoichiometric equation is written below.

$$1CH_4 + 2(O_2 + N_2) \rightarrow 1CO_2 + 2H_2O + 2N_2 \tag{1}$$
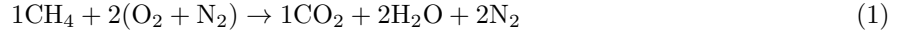
From this equation we know $n_{CH_4} = 1$, $n_{O_2} = 2$, $n_{N_2} = 2$, $n_{CO_2} = 1$, and $n_{H_2O} = 2$. We will also need some physical properties of the various species to solve the enthalpy balance; specifically, we need the heats of formation ($h_{f,m}$) and specific heats at constant pressure ($c_{p,m}$). Note, the subscript "m" indicates the value belongs to an individual species as opposed to the entire mixture. The physical properties can be obtained from a variety of textbook and internet sources which may give slightly different values. The values below are from appendices in "An Introduction to Combustion" by Stephen Turns. Note, the heat of formation of elements in their standard molecular configuration is zero; e.g. hydrogen, oxygen, and nitrogen naturally exist in their diatomic form (H_2, O_2, and N_2), so the heats of formation of these species are zero. Also note that no specific heat values are listed in the table for CH_4 and O_2 because the integrals in which they appear are zero valued due to the bounds of integration (problem statement says initial temperature is 298 K which, conveniently, is the thermodynamic reference temperature).

	$h_{f,m}$ (kJ/kmol)	$c_{p,m}$ (kJ/kmol-K)
CH_4	-74,831	n/a
O_2	0	n/a
N_2	0	34.805
CO_2	-393,546	58.292
H_2O	-241,845	47.103

We can now write and solve the enthalpy balance. The reference temperature (T_{ref}) refers to the thermodynamic standard reference state of 298.15 Kelvin and 1 atmosphere. $T_{initial}$, also sometimes called $T_{reactants}$ is the initial temperature of the reactants before combustion. $T_{adiabatic}$, also sometimes called T_{final} is the adiabatic flame temperature we are solving for.

$$\sum_{Reactants} n_m \left(h_{f,m} + \int_{T_{ref}}^{T_{initial}} c_{p,m}\, dT \right) = \sum_{Products} n_m \left(h_{f,m} + \int_{T_{ref}}^{T_{adiabatic}} c_{p,m}\, dT \right) \tag{2}$$

Since the initial temperature and the reference temperature are the same, we can cross out the integral on the LHS, knowing it will be zero-valued. We then obtain the following where $\Delta T = T_{adiabatic} - T_{ref}$:

$$n_{CH_4} = 1, \ n_{O_2} = 2, \ n_{N_2} = 2, \ n_{CO_2} = 1, \ n_{H_2O} = 2 \tag{3}$$

$$n_{CH_4}(h_{f,CH_4} + 0) + 0 + 0 = n_{CO_2}(h_{f,CO_2} + c_{p,CO_2}\Delta T) + n_{H_2O}(h_{f,H_2O} + c_{p,H_2O}\Delta T) + n_{N_2}(0 + c_{p,N_2}\Delta T) \tag{4}$$

This equation can then be solved for $T_{adiabatic}$.

$$T_{adiabatic} = T_{ref} + \frac{n_{CH_4}h_{f,CH_4} - n_{CO_2}h_{f,CO_2} - n_{H_2O}h_{f,H_2O}}{n_{CO_2}c_{p,CO_2} + n_{H_2O}c_{p,H_2O} + n_{N_2}c_{p,N_2}} = 3,910.829K \tag{5}$$

2. H_2O exists as the major product of combustion for hydrogen and oxygen originally in stoichiometric proportions with no other gas present. Find the fraction of products dissociated to H_2 and O_2 in each of the following conditions for the products:

- (a) 1850 °R and one atmosphere;

- (b) 1850 °R and 10 atmospheres;

- (c) 3100 °R and 10 atmospheres; and

- (d) 1850 °R and one atmosphere but now with hydrogen and air originally.

Solution:
We are given the situation of an ideal reaction producing pure H_2O. The question asks how much of that water would become H_2 and O_2 at the conditions listed. So, using the CSU chemical equilibrium software, we input H and O under "Elements", H_2O with a mole fraction of 1 under "Reactant Mixture Composition", and add H_2 and O_2 in the "Additional Species" boxes. We select **constant pressure and enthalpy** under "Calculation Constraints" because we are dealing with an isobaric process and our energy balance for the adiabatic condition equates to a conservation of total enthalpy. Then we simply input the temperature and pressure conditions given for parts (a-c).

Calculation Constraints

Exactly *one* constraint must be selected for each calculation. Please select one of the following:

- ☐ Constant pressure and temperature
- ☐ Constant volume and temperature
- ☐ Constant temperature and entropy
- ☐ Constant pressure and volume
- ☑ Constant pressure and enthalpy
- ☐ Constant pressure and entropy
- ☐ Constant volume and internal energy
- ☐ Constant volume and enthalpy
- ☐ Constant volume and entropy

Additional Species

Please list any additional species that may be present at equilibrium. It it not necessary to re-enter the reactant species listed above. Only those species listed below and as reactants will be considered in the calculation.

H2	O2	

Elements

Please provide a list of elements present in the gas mixture. Elements present in the database may be found here

H	O				

Reactant Mixture Composition

Species Name	Moles or Mole Fraction
H2O	1

(a) We see the resultant mixture is still mostly H_2O but some has dissociated to H_2 and O_2. The energy expended to dissociate the H_2O molecules results in a slight reduction in temperature from the original 1850 °R, however, it is too small to see. This is why the ideal (no dissociation) adiabatic flame temperature is always be higher than the actual measured (or calculated with detailed chemical kinetics) flame temperature.

	Initial State	Equilibrium State
Pressure (atm)	1.0000E+00	1.0000E+00
Temperature (K)	1.0278E+03	1.0278E+03
Volume (cm³/g)	4.6815E+03	4.6812E+03
Enthalpy (erg/g)	-1.1918E+11	-1.1918E+11
Internal Energy (erg/g)	-1.2392E+11	-1.2392E+11
Entropy (erg/g K)	1.2976E+08	1.2976E+08

	Initial State		Equilibrium State	
	mole fraction	mass fraction	mole fraction	mass fraction
H2O	1.0000E+00	1.0000E+00	1.0000E+00	1.0000E+00
H2	0.0000E+00	0.0000E+00	4.2151E-07	4.7168E-08
O2	0.0000E+00	0.0000E+00	2.1076E-07	3.7434E-07

(b) We see a similar result for case (b); however, the increased pressure aids complete combustion. This means less dissociation takes place and thus the temperature is not reduced as much as in case (a).

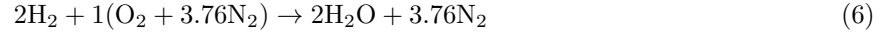|	Initial State	Equilibrium State
Pressure (atm)	1.0000E+01	1.0000E+01
Temperature (K)	1.0278E+03	1.0278E+03
Volume (cm³/g)	4.6815E+02	4.6812E+02
Enthalpy (erg/g)	-1.1918E+11	-1.1918E+11
Internal Energy (erg/g)	-1.2392E+11	-1.2392E+11
Entropy (erg/g K)	1.1914E+08	1.1914E+08

	Initial State		Equilibrium State	
	mole fraction	mass fraction	mole fraction	mass fraction
H2O	1.0000E+00	1.0000E+00	1.0000E+00	1.0000E+00
H2	0.0000E+00	0.0000E+00	1.9565E-07	2.1894E-08
O2	0.0000E+00	0.0000E+00	9.7827E-08	1.7376E-07

(c) Dissociation is highest for case (c). This is because reaction rate increases with temperature according to the Arrhenius law $k(T) = A exp(-E_A/RT)$ where k is the reaction rate constant, A is the pre-exponential factor, T is temperature, E_A is activation energy, and R is the universal gas constant. The higher level of dissociation results in a larger reduction in temperature than in cases (a) or (b).

	Initial State	Equilibrium State
Pressure (atm)	1.0000E+01	1.0000E+01
Temperature (K)	1.7222E+03	1.7197E+03
Volume (cm³/g)	7.8444E+02	7.8344E+02
Enthalpy (erg/g)	-1.0157E+11	-1.0157E+11
Internal Energy (erg/g)	-1.0951E+11	-1.0950E+11
Entropy (erg/g K)	1.3214E+08	1.3214E+08

	Initial State		Equilibrium State	
	mole fraction	mass fraction	mole fraction	mass fraction
H2O	1.0000E+00	1.0000E+00	9.9926E-01	9.9951E-01
H2	0.0000E+00	0.0000E+00	4.9176E-04	5.5042E-05
O2	0.0000E+00	0.0000E+00	2.4588E-04	4.3684E-04

(d) Since the oxidizer is now air, we need a balanced reaction to know the proportions of H_2O and N_2 to put into "Reactant Mixture Composition". Also, because N_2 is in the mix, we need to add N to "Elements".

$$2H_2 + 1(O_2 + 3.76N_2) \rightarrow 2H_2O + 3.76N_2 \tag{6}$$

The result is similar to case (a) but with less dissociation since there is less H_2O to begin with and we did not consider dissociation of N_2.

	Initial State	Equilibrium State
Pressure (atm)	1.0000E+00	1.0000E+00
Temperature (K)	1.0278E+03	1.0278E+03
Volume (cm³/g)	3.4365E+03	3.4363E+03
Enthalpy (erg/g)	-2.4423E+10	-2.4423E+10
Internal Energy (erg/g)	-2.7905E+10	-2.7905E+10
Entropy (erg/g K)	9.6170E+07	9.6170E+07

|	Initial State		Equilibrium State	
	mole fraction	mass fraction	mole fraction	mass fraction
H2O	3.4722E-01	2.5488E-01	3.4722E-01	2.5488E-01
N2	6.5278E-01	7.4512E-01	6.5278E-01	7.4512E-01
H2	0.0000E+00	0.0000E+00	2.0824E-07	1.7105E-08
O2	0.0000E+00	0.0000E+00	1.0412E-07	1.3575E-07

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3. (a) Calculate AF at stoichiometric condition (AF_{st}) for ethyl alcohol C_2H_5OH (aka ethanol) initially at 550 ° R burning in air at 20 atmospheres of pressure. AF is the ratio of mass flow of air to mass flow of fuel. Also, calculate FA = 1/ AF for the same condition.
(b) Calculate AF and $\phi = AF_{st}/AF = FA/FA_{st}$ for ethyl alcohol and 50% excess air at the same conditions.

Solution:
(a) First, balance the stoichiometric reaction (make sure the same number of each element is on the left hand side (LHS) and right hand side (RHS) of the arrow). We obtain Eq. (8).

$$\alpha C_2H_5OH + \beta(O_2 + 3.76N_2) \rightarrow \gamma CO_2 + \delta H_2O + 3.76\beta N_2 \tag{7}$$
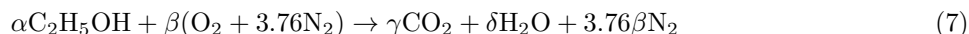
When balancing reactions, it is the proportion that is important not the absolute number of moles. So, we will balance the reaction for $\alpha = 1$. We could also assume $\alpha = $ *any other number* and balance accordingly. Either way, the proportion of various species to each other will be the same. Assuming the fuel coefficient is 1 is usually the easiest.

$$1C_2H_5OH + 3(O_2 + 3.76N_2) \rightarrow 2CO_2 + 3H_2O + 11.28N_2 \tag{8}$$
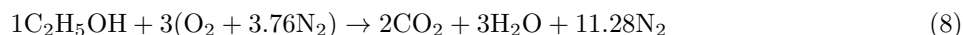
Next, the air/fuel ratio can be calculated. To do this we need the molecular weight of each species and the coefficients from the balanced equation above.

$$A/F = \frac{mass\ of\ air}{mass\ of\ fuel} = \frac{\beta(MW_{O_2} + 3.76MW_{N_2})}{\alpha MW_{C_2H_5OH}} = \frac{3mol(32\frac{g}{mol} + 3.76(28\frac{g}{mol}))}{1mol(46\frac{g}{mol})} = A/F_{st} = 8.953 \tag{9}$$

$$F/A_{st} = \frac{1}{A/F_{st}} = 0.1117 \tag{10}$$

(b) With 50% excess air we need to increase β by 50%, i.e., multiply by 1.5. In our new reaction, $\beta = 4.5$. The product mixture will have the same amount of CO_2 and H_2O because the amount of fuel did not change. However, there will be more N_2 and excess O_2 in the product mixture. The balanced equation is below.

$$1C_2H_5OH + 4.5(O_2 + 3.76N_2) \rightarrow 2CO_2 + 3H_2O + 16.92N_2 + 1.5O_2 \tag{11}$$

A/F for this mixture is calculated in the same way as above just with the different coefficient for air.

$$A/F_{50\%ex} = 13.430 \quad F/A_{50\%ex} = 0.07446 \tag{12}$$

The equivalence ratio is the ratio of the stoichiometric to actual A/F ratios. We know $\phi < 1$ is a lean mixture while $\phi > 1$ is a rich mixture. Since the problem says "excess air", we should expect a lean mixture with $\phi < 1$, and indeed it is. If it were not, a mistake was made somewhere.

$$\phi = \frac{A/F_{st}}{A/F_{50\%ex}} = 0.6666 \tag{13}$$

4. (a) Establish the equations which can be employed for the calculation of the equilibrium composition and the flame temperature when one mole of propane C_3H_8 burns adiabatically at a constant pressure of ten atmospheres. The mixture is lean with 75 % excess air. Both air and fuel enter at a temperature of 800°R. Consider the products to be CO_2, CO, H_2O, H2, O2, and N_2 only. Write all the required equations with known quantities and parameters substituted into the equation. Identify the unknowns. Propane is gaseous at room temperature. Explain what would be different in the analysis if propane entered at a lower temperature in liquid form.
(b) Use the computer software to calculate the final flame temperature and concentrations of the products with the gaseous propane fuel.
(c) For the adiabatic situation with gaseous fuel described in Part a, establish the equations to solve for the theoretical (ideal) temperature and composition. What are the products in this case? Again, write the

necessary equations, identify the known quantities, and identify the unknowns. Solve the equations for the final temperature and composition. Which of the two temperatures from 2b and 2c is larger? Why?

Solution:
(a) Since the problem tells us "excess air", we need to do what we did in the last problem: balance the stoichiometric reaction, multiply the air coefficient by 1.75, then balance this new equation to get our actual reaction. This part will be brief since it was explained in the last problem and the process is the same. First, balance the stoichiometric equation which gives us:

$$1C_3H_8 + 5(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2O + 18.8N_2 \tag{14}$$
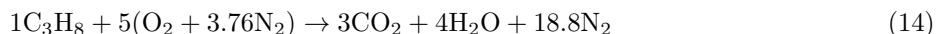
Now, multiply the air coefficient by 1.75 (so instead of 5 it is 8.75), and set up the balance equations for this new reaction including the additional species listed in the problem statement. Note, the question asks us only to "establish" the equations, not solve them (we cannot actually solve the system below because there are more unknowns than equations.)

$$1C_3H_8 + 8.75(O_2 + 3.76N_2) \rightarrow \gamma CO_2 + \delta H_2O + \epsilon CO + \zeta H_2 + \eta N_2 + \theta O_2 \tag{15}$$
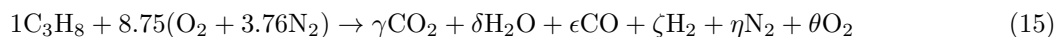
$$C : 3 = \gamma + \epsilon$$

$$H : 8 = 2\delta + 2\zeta$$

$$O : 17.5 = 2\gamma + \delta + \epsilon + 2\theta$$

$$N : 32.9 = \eta$$

For chemical equilibrium of part (a), we have two dissociation reactions which each have equilibrium constants. These reactions and their equilibrium constants are written in the forms:

$$\nu_a A + \nu_b B \leftrightarrow \nu_c C + \nu_d D \tag{16}$$

$$K_p = K_c(RT)^{\nu_d + \nu_c - \nu_b - \nu_a} \tag{17}$$

The two dissociation reactions with their equilibrium constants are:

$$CO_2 \leftrightarrow CO + \frac{1}{2}O_2 \tag{18}$$

$$K_{p18} = K_{c18}(RT_{ad})^{1/2} \tag{19}$$

$$H_2O \leftrightarrow H_2 + \frac{1}{2}O_2 \tag{20}$$

$$K_{p20} = K_{c20}(RT_{ad})^{1/2} \tag{21}$$

For flame temperature, we would solve the total enthalpy conservation equation used in prior problems (Eq. (2)) written again below.

$$\sum_{Reactants} n_m \left(h_{f,m} + \int_{T_{ref}}^{T_{initial}} c_{p,m} \, dT \right) = \sum_{Products} n_m \left(h_{f,m} + \int_{T_{ref}}^{T_{adiabatic}} c_{p,m} \, dT \right) \tag{22}$$

If propane entered in liquid form, it would have to be vaporized. This requires energy and would and is accounted for by including the "heat of vaporization" in the energy balance. Heats of vaporization can be found online or in textbooks.

(b) Using the reactant mixture of Eq. (15) and conditions given in the problem statement, the CSU equilibrium solver returns the desired parameters.

	Initial State	Equilibrium State
Pressure (atm)	1.0000E+01	1.0000E+01
Temperature (K)	4.4443E+02	1.7657E+03
Volume (cm³/g)	1.2486E+02	5.0765E+02
Enthalpy (erg/g)	7.0819E+08	7.0819E+08
Internal Energy (erg/g)	-5.5694E+08	-4.4356E+09
Entropy (erg/g K)	6.6543E+07	8.4587E+07

	Initial State		Equilibrium State	
	mole fraction	mass fraction	mole fraction	mass fraction
C3H8	2.3447E-02	3.5399E-02	0.0000E+00	0.0000E+00
O2	2.0516E-01	2.2476E-01	8.5917E-02	9.6334E-02
N2	7.7140E-01	7.3984E-01	7.5372E-01	7.3984E-01
CO2	0.0000E+00	0.0000E+00	6.8718E-02	1.0597E-01
H2O	0.0000E+00	0.0000E+00	9.1634E-02	5.7844E-02
CO	0.0000E+00	0.0000E+00	1.0457E-05	1.0263E-05
H2	0.0000E+00	0.0000E+00	3.8111E-06	2.6921E-07

(c) For the ideal case, there is no dissociation so we can remove CO, H_2, and O_2 from the chemical reaction (Eq. (15)). Since there are now 3 fewer unknowns, we can actually solve it.

$$1C_3H_8 + 8.75(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2O + 32.9N_2 + 3.75O_2 \tag{23}$$
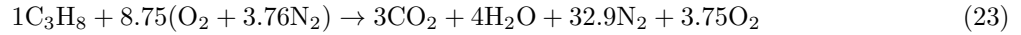
$$n_{C_3H_8} = 1, \ \ n_{O_2}^R = 8.75, \ \ n_{N_2}^R = n_{N_2}^P = 32.9, \ \ n_{CO_2} = 3, \ \ n_{H_2O} = 4, \ \ n_{O_2}^P = 3.75 \tag{24}$$

We can now write the energy balance and solve the equation.

$$\sum_{Reactants} n_m \left(h_{f,m} + \int_{T_{ref}}^{T_{initial}} c_{p,m} \, dT \right) = \sum_{Products} n_m \left(h_{f,m} + \int_{T_{ref}}^{T_{adiabatic}} c_{p,m} \, dT \right) \tag{25}$$

$$T_{ad} = T_{ref} + \frac{n_{C_3H_8}h_{f,C_3H_8} - n_{CO_2}h_{f,CO_2} - n_{H_2O}h_{f,H_2O} + (T_i - T_{ref})(n_{C_3H_8}c_{p,C_3H_8} + n_{O_2}^R c_{p,O_2} + n_{N_2}^R c_{p,N_2})}{n_{CO_2}c_{p,CO_2} + n_{H_2O}c_{p,H_2O} + n_{O_2}^P c_{p,O_2} + n_{N_2}^P c_{p,N_2}} \tag{26}$$

The answer will vary depending on the values used for c_{p_m}. Using constants again from "An Introduction to Combustion" as well as "Engineering Toolbox" (shown in the table below) we get:

	$h_{f,m}$ (kJ/kmol)	$c_{p,m}$ (kJ/kmol-K)
C_3H_8	-103,847	73.920
O_2	0	34.880
N_2	0	32.676
CO_2	-393,546	54.299
H_2O	-241,845	41.103

$$T_{ad} = 1770.22 \ K \ \ or \ \ T_{ad} = 3186.40°R \tag{27}$$

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This temperature is slightly higher than the temperature from (b) because there is no dissociation here. Notice, the two temperatures are relatively close which suggests dissociation is not strong in this reaction.

5. Do a preliminary design on a rocket combustor. A peak temperature of 4500 °R is desired and the average molecular weight of the hot products should be no greater than 27 g/mol. Choose an appropriate fuel that will burn with oxygen (O_2). Candidates are ethanol (C_2H_5OH), hydrogen (H_2), and methane (CH_4). Design to have the theoretical (ideal) flame temperature (without dissociation) at 4500 °R. Determine the proper mixture ratio of fuel to oxygen for that case. Then, calculate the equilibrium temperature which will be a little lower. Estimate the mass fractions of the products at equilibrium. Determine the average molecular weight of the equilibrium products.

Solution:
It is best to start this problem with physical intuition based on the two constraints, molecular weight less than 27 g/mol and ideal adiabatic flame temperature of 4500 °R (2500 K). Because ideal adiabatic flame temperature of a stoichiometric reaction with any of these fuels will be roughly 4000 K - 5000 K, we know we will have to burn at a non-stoichiometric condition (that is ether excess fuel (rich) or excess oxygen (lean)). Note that in these design problems, there are many combinations that will satisfy the requirements so there is not one correct answer.

We will try methane (CH_4). Balancing the stoichiometric equation gives us a starting point for the chemical equilibrium software. The balanced equation is below.

$$1CH_4 + 2O_2 \rightarrow 1CO_2 + 2H_2O \tag{28}$$

Using these reactants in the software and choosing an initial temperature and pressure of 300 K and 30 atm, respectively, gives us a temperature of 5198.7 K which is too high. So, we will have to increase the oxidizer or fuel percentage to bring the temperature down. We will choose to increase the fuel percentage because excess (O_2) often causes parts the engine to burn up (pretty much everything, including metals, likes to burn in a hot environment with pure O_2). We iteratively increase the fuel percentage until the temperature is 4500 °R (2500 K) and find that the non-stoichiometric reactant mixture below produces the correct temperature.

$$3.805CH_4 + 2O_2 \tag{29}$$

	Initial State	Equilibrium State
Pressure (atm)	3.0000E+01	3.0000E+01
Temperature (K)	3.0000E+02	2.4999E+03
Volume (cm³/g)	3.8095E+01	3.1743E+02
Enthalpy (erg/g)	-2.2762E+10	-2.2762E+10
Internal Energy (erg/g)	-2.3920E+10	-3.2411E+10
Entropy (erg/g K)	7.8867E+07	1.3428E+08

	Initial State		Equilibrium State	
	mole fraction	mass fraction	mole fraction	mass fraction
CH4	6.5547E-01	4.8819E-01	4.8320E-01	3.5989E-01
O2	3.4453E-01	5.1181E-01	1.0018E-09	1.4883E-09
CO2	0.0000E+00	0.0000E+00	1.7227E-01	3.5196E-01
H2O	0.0000E+00	0.0000E+00	3.4453E-01	2.8815E-01

Next, we have to check if the molecular weight is below 27 g/mol. Molecular weight of a mixture is defined by Eq. (30) where X_m is the mole fraction of species m and MW_m is the molecular weight of species m.

$$MW_{mix} \equiv \sum_{m=1:N} X_m MW_m \tag{30}$$

Using the mole fractions from the software under "Equilibrium State" we find the mixture molecular weight is $MW_{mix} = 21.5134 \ g/mol$, which satisfies the requirement. If it did not, we would have to go back and adjust the mixture composition. The question also asks for the mass fractions of products which are also returned by the software. We could add dissociation species to the "Additional Species" boxes and see what the actual temperature and composition is. The actual temperature would be lower.