Gibbs Free Energy Minimization

Assignment Report

Transatmospheric and Space Propulsion AERO 4442

Carleton University

Mechanical and Aerospace Engineering Department

Prepared By: Antoine Brule

Report Submitted: March 14, 2025

1   Introduction

Many modern propulsion systems employ some form of combustion to convert chemical energy into a form of useful energy. For the propulsion systems of jet aircraft, and spacecraft, it is converted into thermal energy. Since the post-combustion temperature is a direct measure of how much energy is released through combustion, calculating it value is of great interest. Through the application of the Gibbs energy minimization technique the post-combustion mixture composition and temperature can be determined for a large variety of pre-combustion mixtures. This report contains the theory and equations used to develop a program to find the equivalence ratio at a specified equilibrium temperature using Gibbs free energy minimization. Additionally this report covers the methodology of the code and results for the combustion of oxygen and hydrogen along with comparisons to NASA's CEA.

2   Nomenclature

Symbol	Name	Units
$\frac{f}{o}$	Fuel to oxidizer ratio	$\frac{mol}{mol}$
$(\frac{f}{o})_{st}$	Stoichiometric fuel to oxidizer ratio	$\frac{mol}{mol}$
ϕ	Equivalence Ratio	N/A
G	Gibbs free energy	J
$\tilde{g}_k$	Gibbs free energy per mole of species k	$\frac{j}{kmol}$
σ_k	Number of moles of species k	mol
σ_m	Number of moles of the mixture	mol
$\tilde{h}_k$	Enthalpy per mole of species k	J
T	Equilibrium combustion temperature	K
p	Combustion pressure	pa
p_{ref}	Reference Pressure	101325 pa
$\tilde{s}_k$	Entropy per mole of species k	$\frac{J}{K}$
$\Re$	Universal Gas Constant	$8314 \frac{J}{kmolK}$
η_{ik}	Number of atoms i per species k	N/A
$\bar{B}_i$	Number of moles of atom i	mol
N_A	Avogadro's number	6.022×10^{23}
H	Total Enthalpy	J
α_i	Lagrange multiplier of atom i over $\Re T$	$\frac{j}{kmols}$
n_a	Number of different atoms under consideration	N/A
n_s	Number of different spices under consideration	N/A
$(\tilde{c_p})_k$	Specific heat per mole of species k	J

Table 1: List of Symbols

3   Theory

The equations and theory presented in this section make the following assumptions. The fuel and oxidizer mixture has enough time to react and reach chemical equilibrium. The

pressure is kept constant during the combustion process. The process has no friction losses and there is no heat transfer out of the control volume, enthalpy is conserved through the process. No ions are formed during the combustion process and the post-combustion species are all gaseous.

This report uses the equivalence ratio defined below to express the ratio of fuel to oxidizer.

$$\phi = \frac{\frac{f}{o}}{(\frac{f}{o})_{st}} \tag{1}$$

The Gibbs free energy of a mixture of gasses, what we are trying to minimize, can be obtained using equation 2 below.

$$G = \sum_k \tilde{g}_k \sigma_k \tag{2}$$

The molar Gibbs free energy of each species can be obtained with equation 3 below.

$$\tilde{g}_k = \tilde{h}_k(T, p_{ref}) - T\tilde{s}_k(T, p_{ref}) + \Re T ln\left(\frac{\sigma_k}{\sigma_m}\right) + \Re T ln\left(\frac{p}{p_{ref}}\right) \tag{3}$$

This requires knowing the molar enthalpy and entropy which can be obtained from equations 4 and 5

$$\tilde{h}_k = \Re T\left(-a_1 T^{-2} + a_2 ln(T)/T + a_3 + a_4 T/2 + a_5 T^2/3 + a_6 T^3/4 + a_7 T^4/5 + b_1/T\right) \tag{4}$$

$$\tilde{s}_k = \Re\left(-a_1 T^{-2}/2 + a_2 T^{-1} + a_3 lnT + a_4 T + a_5 T^2/2 + a_6 T^3/3 + a_7 T^4/4 + b_2\right) \tag{5}$$

The molar specific heat can also be obtained with equation 6 below.

$$(\tilde{c}_p)_k = \Re\left(a_1 T^{-2} + a_2 T^{-1} + a_3 + a_4 T + a_5 T^2 + a_6 T^3 + a_7 T^4\right) \tag{6}$$

The a and b coefficients from equations 4, 5, and 6 can be obtained from Reference [1] and [4]. The coefficients are discussed in more detail in section 4.3.

During the combustion process the hydrogen and oxygen containing molecules will react with each other and form new molecules. Other species present in the mixture can also react or dissociate if the temperature is high enough. The disassociation and formation of new species will be determined by whether or not it decreases the total Gibbs free energy. This will occur as long as the total number of atoms of each element is conserved.

$$\sum_k \eta_{ik} \sigma_k = \frac{B_i}{N_A} = \bar{B}_i \tag{7}$$

Similarly, the total number of moles of the mixture should equal the sum of the number of moles of each species.

$$\sum_k \sigma_k = \sigma_m \tag{8}$$

In addition since energy is conserved during the combustion process this means that the total enthalpy of the pre-combustion mixture must equal the total enthalpy of the post-combustion mixture.

$$\sum_k \sigma_k \tilde{h}_k = H \tag{9}$$

At equilibrium the change in total Gibbs energy will be zero since it will have reached its global minima. Rearranging and setting equation 2 to zero gives the first condition for equilibrium and taking the derivative with respect to time of equation 7.

$$\sum_k \tilde{g}_k d\sigma_k = 0$$

$$\sum_k \eta_{ik} d\sigma_k = 0$$

By applying the method of Lagrange Multipliers to these two equations, using the second as a side constraint, we obtain the following set of equations for each species under consideration.

$$\frac{\tilde{g}_k}{\Re T} - \sum_i \alpha_i \eta_{ik} = 0$$

From this and equations 7, 8, 9 we obtain a system of equations that we can solve through iteration. The number of equations in this system is equal to the number of species under consideration plus the number of elements under consideration. Most combustion reactions have a most 4 elements involved (H,O,N,C) but can have many more possible post-combustion species. To reduce the size of the system of equations that needs to be solved Newton's method is used which when put into matrix form yields the matrices 10 and 11. These are the reduced Gibbs iteration equations. The solution vector, X, can be obtain by finding the solution to 13.

$$A = \begin{bmatrix}
\sum_k \eta_{1k}\sigma_k\eta_{1k} & \sum_k \eta_{1k}\sigma_k\eta_{2k} & \cdots & \sum_k \eta_{1k}\sigma_k\eta_{n_ak} & \sum_k \eta_{1k}\sigma_k & \sum_k \eta_{1k}\sigma_k\frac{\tilde{h}_k}{\Re T} \\
\sum_k \eta_{2k}\sigma_k\eta_{1k} & \sum_k \eta_{2k}\sigma_k\eta_{2k} & \cdots & \sum_k \eta_{2k}\sigma_k\eta_{n_ak} & \sum_k \eta_{2k}\sigma_k & \sum_k \eta_{2k}\sigma_k\frac{\tilde{h}_k}{\Re T} \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\sum_k \eta_{n_ak}\sigma_k\eta_{1k} & \sum_k \eta_{n_ak}\sigma_k\eta_{2k} & \cdots & \sum_k \eta_{n_ak}\sigma_k\eta_{n_ak} & \sum_k \eta_{n_ak}\sigma_k & \sum_k \eta_{n_ak}\sigma_k\frac{\tilde{h}_k}{\Re T} \\
\sum_k \eta_{1k}\sigma_k\frac{\tilde{h}_k}{\Re T} & \sum_k \eta_{2k}\sigma_k\frac{\tilde{h}_k}{\Re T} & \cdots & \sum_k \eta_{n_ak}\sigma_k\frac{\tilde{h}_k}{\Re T} & \sum_k \sigma_k\frac{\tilde{h}_k}{\Re T} & \sum_k \sigma_k\left[\frac{(\tilde{c}_p)_k}{\Re} + \left(\frac{\tilde{h}_k}{\Re T}\right)^2\right] \\
\sum_k \eta_{1k}\sigma_k & \sum_k \eta_{2k}\sigma_k & \cdots & \sum_k \eta_{n_ak}\sigma_k & \sum_k \sigma_k - \sigma_m & \sum_k \sigma_k\frac{\tilde{h}_k}{\Re T}
\end{bmatrix} \tag{10}$$

$$C = \begin{bmatrix}
\bar{B}_1 + \sum_k \eta_{1k}\sigma_k\left(\frac{\tilde{g}_k}{\Re T} - 1\right) \\
\bar{B}_2 + \sum_k \eta_{2k}\sigma_k\left(\frac{\tilde{g}_k}{\Re T} - 1\right) \\
\cdots \\
\bar{B}_{n_a} + \sum_k \eta_{n_ak}\sigma_k\left(\frac{\tilde{g}_k}{\Re T} - 1\right) \\
\frac{H}{\Re T} + \sum_k \sigma_k\frac{\tilde{h}_k}{\Re T}\left(\frac{\tilde{g}_k}{\Re T} - 1\right) \\
\sigma_m + \sum_k \sigma_k\left(\frac{\tilde{g}_k}{\Re T} - 1\right)
\end{bmatrix} \tag{11}$$

$$X = \begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_{n_a} \\ \Delta ln\sigma_m \\ \Delta lnT \end{bmatrix} \tag{12}$$

$$[A][X] = [C] \tag{13}$$

After obtaining the solution vector, the natural logarithm of the change in moles of each species can be obtain with equation 14 below.

$$(\Delta ln\sigma_k) = (\Delta ln\sigma_m) + \left(\frac{\tilde{h}_k}{\Re T}\right)(\Delta lnT) - \frac{\tilde{g}_k}{\Re T} + \sum_i \alpha_i \eta_{ik} \tag{14}$$

Before obtaining the new values required to perform the next iteration the under-relaxation parameter must be calculated using equations 15, 16, and 17. For species with more than $1 \times 10^{-8} kmols$ use equation 15, otherwise use 16.

$$\beta_1 = \frac{2}{max(|\Delta lnT|, |\Delta ln\sigma_m)|, |\Delta ln\sigma_k|} \tag{15}$$

$$\beta_2 = \frac{ln(10^{-4}) - ln(\sigma_k) + ln(\sigma_m)}{\Delta ln\sigma_k - \Delta ln\sigma_m} \tag{16}$$

$$\beta = min(1, \beta_{1,min}, \beta_{2,min}) \tag{17}$$

With the under-relaxation parameter calculated the initial conditions for the next iteration can be calculated using equations 24, 19, and 20.

$$ln(T_{new}) = ln(T_{old}) + \beta \Delta ln(T) \tag{18}$$

$$ln(\sigma_{m_{new}}) = ln(\sigma_{m_{old}}) + \beta \Delta ln(\sigma_m) \tag{19}$$

$$ln(\sigma_{k_{new}}) = ln(\sigma_{k_{old}}) + \beta \Delta ln(\sigma_k) \tag{20}$$

The iterations process is repeated until all the convergence conditions are met, equations 21,22, 23, and 24 [2].

$$\frac{\sigma_k |\Delta ln\sigma_k|}{\sum_k \sigma_k} < 0.5 * 10^{-5} \tag{21}$$

$$\frac{\sigma_m |\Delta ln\sigma_m|}{\sum_k \sigma_k} < 0.5 * 10^{-5} \tag{22}$$

$$|\bar{B}_i| - \sum_k \eta_{ik} \sigma_{m_{new}} < max(\bar{B}) \cdot 10^{-6} \tag{23}$$

$$|\Delta lnT| < 1.0 * 10^{-4} \tag{24}$$

4   Methodology

The program is split into several function files. The first is solve.m which is performs the Gibbs energy minimization for a given set of initial conditions. To accomplish this it calls gibbs.m, specificHeat.m, entropy.m, and enthalpy.m which are used to obtain the molar enthalpies, specific heat, entropy, and gibbs free energy of each species for a given pressure and temperature. To avoid calculating these values more then once per iteration for each species the gibbs.m functions also returns the enthalpy, specific heat, and entropy of the species.

A warper function, TempFinder.m, is used to prepare the inputs for solve.m. Through successive calls of solve.m, TempFinder.m is able to determine the post-combustion species and temperature of a given equivalence ratio. Using the change in fuel to oxidizer ratio versus the change in equilibrium temperature between iterations the equivalence ratio which produces the desired equilibrium temperature can be determined rather quickly. To prepare the inputs for solve.m the wrapper uses speciesLoader.m to load the species data from a .dat file and STbalance.m to find the stoichiometric fuel to oxidizer ratio for any hydrocarbon combustion reaction. The function enthalpy.m is also used to find the total enthalpy of the pre-combustion mixture before each call of solve.m. Figure 1 below shows a diagram of which functions call which.
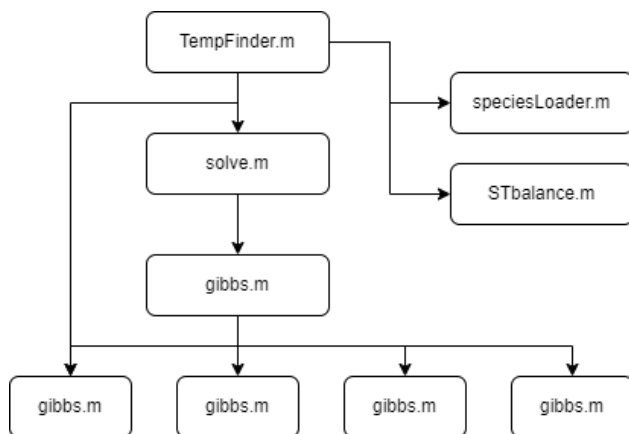

Figure 1: Function Heiarchy

4.1   Species Loader

The programs comes with a data file containing 163 possible combustion reagents and products and a .mat file containing 23 species from Reference [1]. More are included in the data file but are for condensed states of species which are not compatible with the program at this time. The species data was obtained from Reference [4] which gives the data as plain text. For each species a "card" contains the relevant data. Table 2 below explains the format of the data cards.

Figure 2: Species Data Card Format [5]

Record	Contents	FORTRAN format	Columns
1	Species name or formula	A16	1 to 16
	Comments and data sources	A62	19 to 80
2	Number of T intervals	I2	1 to 2
	Reference date code	A6	4 to 9
	Chemical formula—symbols (all capitals) and numbers	5(A2, F6.2)	11 to 50
	Zero for gas; nonzero for condensed[a]	I2	51 to 52
	Molecular weight	F13.7	53 to 65
	Heat of formation at 298.15 K, J/mol	F15.5	66 to 80
3	Temperature range	2F11.3	1 to 22
	Number of coefficients for $C_p^o(T)/R$ (always seven)	I1	23
	T exponents in empirical equation for $C_p^o(T)/R$ [always $-2, -1, 0, 1, 2, 3, 4$; see eq. (1)]	8F5.1	24 to 63
	$H^o(298.15) - H^o(0)$ J/mol, if available	F15.3	66 to 80
4	First five coefficients for $C_p^o(T)/R$, eq. (1)	5D16.9	1 to 80
5	Last two coefficients for $C_p^o(T)/R$, eq. (1)	2D16.9	1 to 32
	Integration constants b_1 and b_2, eqs. (2) and (3)	2D16.9	49 to 80
-	Repeat 3, 4, and 5 for each interval	---------	----------

[a] Condensed phases are numbered in increasing order by temperature.

The data "card" for titanium nitride is given below as an example in Figure 3.

```
      1234567890123456789012345678901234567890123456789012345678901234567890123456789 0
               10        20        30        40        50        60        70        80

1    TiN(cr)           Chase,1998 pp1612-4.                                            1
2     2 j 6/68 TI  1.00N   1.00    0.00     0.00     0.00 1     61.87374    -337648.800  2
3       200.000    800.0007 -2.0 -1.0   0.0   1.0   2.0   3.0   4.0   0.0      5487.000  3
4    -5.479117220D+05 9.328691110D+03-6.386263890D+01 2.429925456D-01-4.304234520D-04  4
5     3.792645100D-07-1.317412256D-10            -8.424256140D+04 3.392988560D+02       5
6       800.000   3220.0007 -2.0 -1.0   0.0   1.0   2.0   3.0   4.0   0.0      5487.000  6
7    -3.656247060D+05 1.265730431D+03 3.831711190D+00 1.632900455D-03-1.062786626D-07  7
8     1.310931390D-11-5.770548410D-16            -5.027654400D+04-1.652632899D+01       8
9    TiN(L)            Chase,1998 pp1612-4.                                            9
10    1 j 6/68 TI  1.00N   1.00    0.00     0.00     0.00 2     61.87374    -337648.800  10
11     3220.000   6000.0007 -2.0 -1.0   0.0   1.0   2.0   3.0   4.0   0.0      5487.000  11
12    0.000000000D+00 0.000000000D+00 7.548249987D+00 0.000000000D+00 0.000000000D+00  12
13    0.000000000D+00 0.000000000D+00            -3.626039860D+04-3.958296649D+01       13

      1234567890123456789012345678901234567890123456789012345678901234567890123456789 0
               10        20        30        40        50        60        70        80
```

Figure 3: Titanium Nitride Data Card [5]

The speciesLoader.m function parses all data cards of the gaseous species into a structure array that can be readily interpreted by the rest of the program. Table 2 gives the fields of the structure array with a brief description and units.

Feild	Description	Type
Name	Name (chemical formula) of the species	str
Intervals	Valid Temperature Intervals for the coefficients	3 by 2 double
Atoms	String array conaining the atoms of the species	1 by n str
Eta	Vector which contains the number of each atom in the species	1 by n double
Phase	Zero if gaseous other wise non zero	double
Weight	Molecular weight of the species	double $\frac{g}{mol}$
h_f	Heat of formation at 295.15K	double $\frac{j}{mol}$
h_f0	Difference between the heat of formation at 295.15 and 0K	double $\frac{j}{mol}$
Coefficients	Coefficients matrix, one row per temperature interval [a1 a2 a3 a4 a5 a6 a7 b1 b2]	x by 9 double

Table 2: Species Structure Array Fields

4.2 Combustion Equation Balancer

Determining the equivalence ratio of an arbitrary fuel and oxidizer mixture requires knowing the stoichiometric fuel-oxidizer ratio of the specific fuel and oxidizer mixture. Since there is a very large number of possible fuel and oxidizer mixtures, with a corresponding stoichiometric fuel to oxidizer ratio. The stoichiometric fuel to oxidizer ratio can be determined manually by balancing the complete combustion equation of the fuel and oxidizer mixture. However, this process can be quite tedious to do by hand depending on the number of combustion reactants. For this reason the program includes a combustion balancer which can obtain the stoichiometric fuel to oxidizer ratio for any mixture containing hydrogen, oxygen, carbon, and nitrogen. Any other atoms would not be considered properly unless the compound containing extra atom does not react into any other compound containing hydrogen, oxygen, carbon, or nitrogen.

The first step of this process is to determine the number of H,N,C,O atoms in the fuel and oxidizer mixtures. These values are stored in two column vectors. The next step is to find the values of a,b,c,d,e in the equation below.

$$a(Fuel) \ + b(Oxidizer) \rightarrow cH2O + dN2 \ + eCO2 \tag{25}$$

Where Fuel and Oxidizer are the vectors from the first step. Next, the following system of equations is formed.

$$
\begin{aligned}
H &: aFuel_H + bOxidizer_H - c2 = 0 \\
O &: aFuel_O + bOxidizer_O - c - e2 = 0 \\
N &: aFuel_N + bOxidizer_N - d2 = 0 \\
C &: aFuel_C + bOxidizer_C - e = 0
\end{aligned}
\tag{26}
$$

The system of equations is converted into matrix form and the matrix is reduced to row-echelon form. The stoichiometric fuel to oxidizer ratio is obtained from $\frac{a}{b}$.

4.3 Thermodynamic Data Functions

To obtain the molar Gibbs free energy of each species the molar enthalpy, entropy, and specific heat of each species is also required. The enthalpy, entropy, and specific heat of each species can be obtained with equations 6,4, and 5 and the corresponding coefficients from References [1] or [4]. Reference [1] uses an older format for the thermodynamic properties coefficients that are missing the leading two coefficients from equations 6,4,5. By setting the two leading coefficients of equations 6,4, and 5 to zero the coefficients from [1] can be used as normal.

4.4 Solver

The solve.m function takes in the total mixture enthalpy, a vector containing the number of each atom, a matrix that contains the number of atoms contained in each species, and a matrix containing the thermodynamic property equation coefficients of each species along with some constants. Once the convergence process has completed it returns a vector contain the number of moles of each post combustion species, the total number of moles of post-combustion species, the equilibrium combustion temperature, and the number of iteration required to achieve convergence.

The first step of the iteration process is to calculate the molar Gibbs free energy, enthalpy and specific heat of each species using the Gibbs function which will return those three values. Then the A matrix from equation 10 and C vector from equation **??** are constructed. These are built to match the number of unique atoms under consideration so that the solve.m function can handle any combination of atoms. From A and C the solution vector can now be obtained using equation 13. From this the natural logarithm of the change in moles of each species can be calculated using equation 14.

The next step is to calculate the under relaxation parameter using equation 17. The under relaxation parameter is used to ensure that the iteration process remains stable and does not suffer from numerical instability [1]. For each species, calculate β_1 using equation 15 if the number of moles of that species is greater than $1 \times 10^-8 \ kmols$. Otherwise calculate β_2 for that species using equation 16. Using the calculated β value and equations 24, 19, and 20 the new equilibrium combustion temperature, total moles of the mixture, and the number of moles of each species.

The final step of the iteration process is to check for convergence. To ensure that proper convergence is achieved four convergence tests are used as recommended by Reference [2]. The iteration process will only end once equations 21, 22, 23, and 24 are satisfied or the number of iterations exceeds 100. If the number of iterations exceeds 100 the function will throw an error indicating that it has failed to converge.

5 Results

Results are presented for calculations performed using coefficients from Reference [1] and [4] which will be referred to as case 1 and case 2 respectively. The combustion pressure for all cases is 10atm and the pre-combustion mixture temperature is 298.15K. The fuel is H_2 and

the oxidizer is O_2 for all reported results. The equilibrium post combustion temperature of oxygen and hydrogen is plotted for a range of equivalence ratios in Figure 4 below.
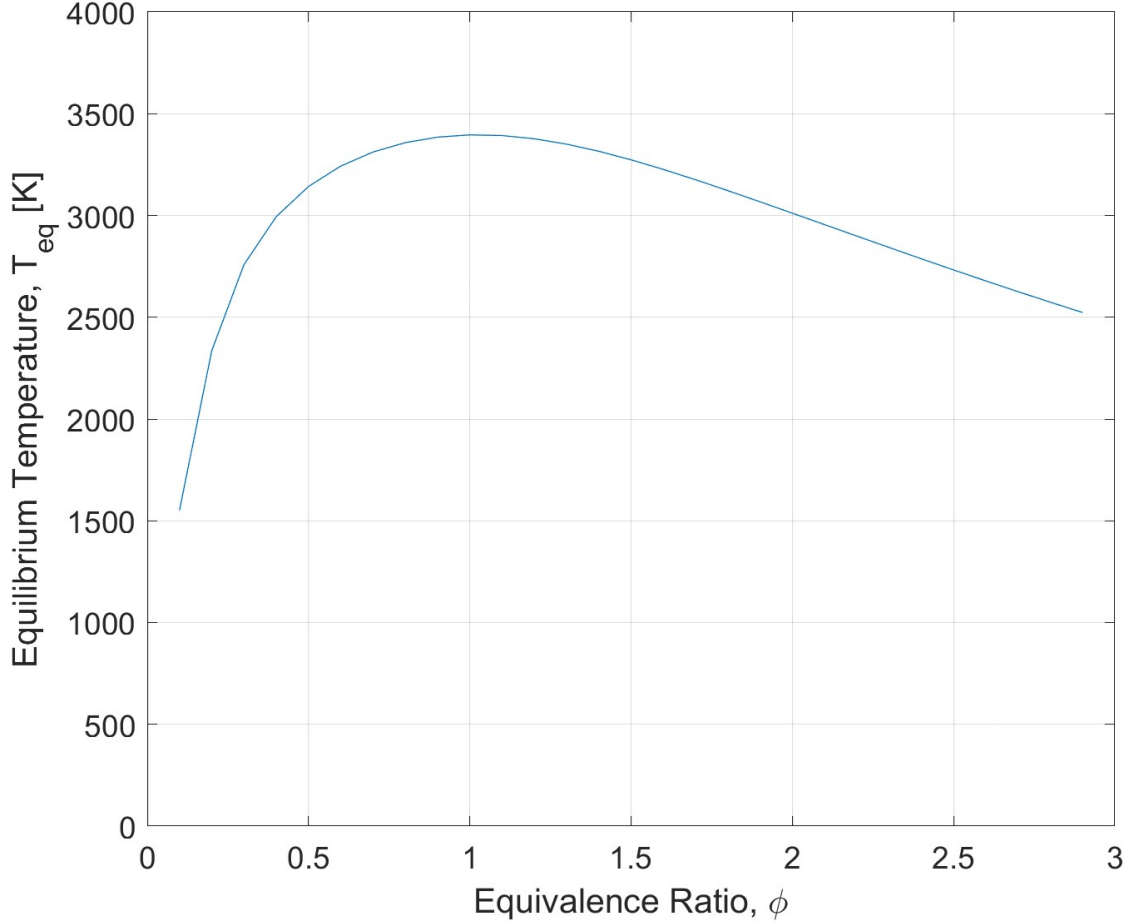

Figure 4: Equilibrium Temperature of Hydrogen/Oxygen Combustion

The calculated peak temperature is around 3390K for both cases which occurs at an equivalence ratio of one, as expected. The equivalence ratios that yield a post-combustion temperature of 3383K are tabulated for both cases in Table 7 below.

Case	ϕ_1	ϕ_2
1 [1]	0.89	1.17
2 [4]	0.92	1.14

Table 3: Equivalence Ratios which yield 3383K

The difference between the two sets of coefficients is fairly small with a relative error of approximately 3% for both equivalence ratios. The mass fractions of post-combustion species with mass fraction greater than 0.01% for both cases are plotted in figures 5 and 6.
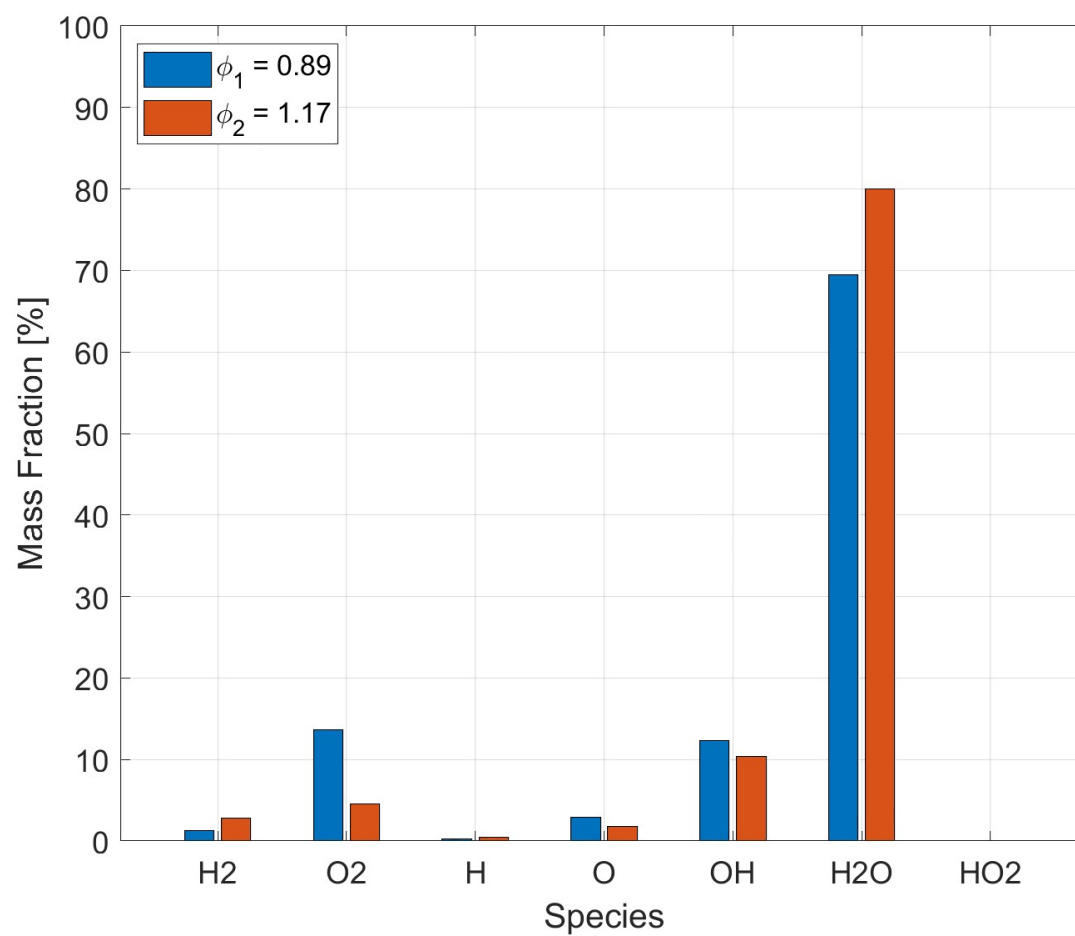
9

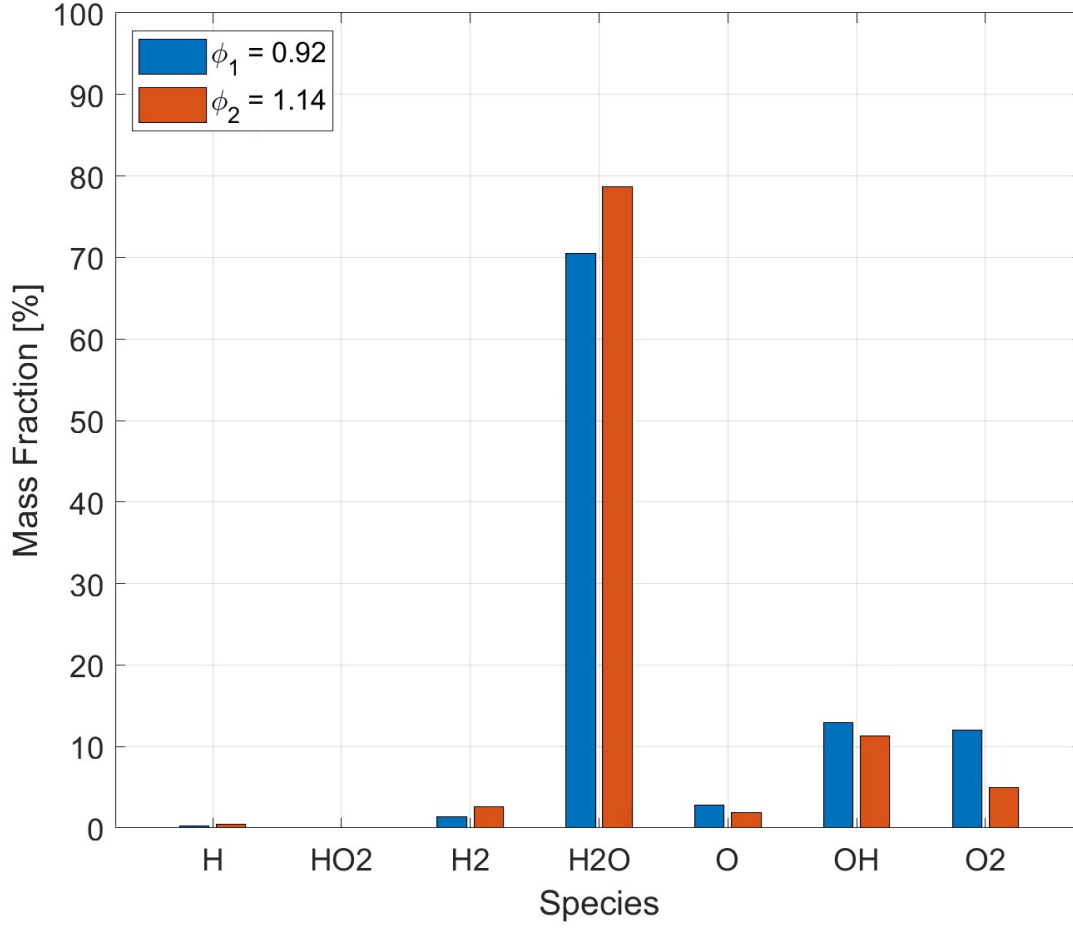Figure 5: Post-combustion Species Mass Fraction for Case 1

Figure 6: Post-combustion Species Mass Fraction for Case 2

The results of figures 5 and 6 above are tabulated in Table 4 below.

Species	Case 1		Case 1	
	ϕ_1	ϕ_2	ϕ_1	ϕ_2
H2O	69.47%	80.01%	70.52%	78.72%
OH	12.27%	10.37%	12.93%	11.31%
O2	13.68%	4.5%	12.01%	5.00%
H2	1.3%	2.82%	1.42%	2.61%
O	2.95%	1.83%	2.79%	1.91%
H	0.28%	0.45%	0.3%	0.43%
HO2	0.03%	0.01%	0.03%	0.02%

Table 4: Post-combustion Species Mass Fraction for both Cases

The presence of OH,H, and O in the post-combustion species is to be expected since the equilibrium temperature exceeds 3000k. The difference between the two cases is rather small

with only a few percent difference at the worst. The largest relative error is with the mass fraction of HO_2 at ϕ_2 since its mass fraction is so small and gets truncated.

5.1 Comparison with NASA CEA

To verify that the output of the code was accurate it was compared to NASA CEA [3] at the equivalence points that yielded a post-combustion equilibrium temperature of 3383K. The comparison of the post-combustion temperature for a range of equivalences ratio is tabulated below in Tables 8 and 9.

Equivalence Ratio	Case 1 [1]	CEA [3]	Relative Error
0.2	2331.45	2335.55	-0.18%
0.6	3235.92	3242.76	-0.21%
0.9	3379.58	3384.94	-0.16%
1	3390.58	3395.9	-0.16%
1.1	3387.14	3392.62	-0.16%
1.4	3309.38	3315.56	-0.19%
1.8	3117.21	3122.01	-0.15%
2.2	2895.49	2898.64	-0.11%
2.6	2676.39	2678.43	-0.08%
3	2472.64	2473.98	-0.05%

Table 5: Equilibrium Temperature Comparison with NASA CEA for CASE 1

Equivalence Ratio	Case 2 [4]	CEA [3]	Relative Error
0.2	2331.45	2332.08	-0.03%
0.6	3235.92	3236.15	-0.01%
0.9	3379.58	3379.76	-0.01%
1	3390.58	3390.75	-0.01%
1.1	3387.14	3387.31	-0.01%
1.4	3309.38	3309.6	-0.01%
1.8	3117.21	3117.55	-0.01%
2.2	2895.49	2895.96	-0.02%
2.6	2676.39	2676.98	-0.02%
3	2472.64	2473.33	-0.03%

Table 6: Equilibrium Temperature Comparison with NASA CEA for CASE 2

As shown above in both cases the results from both cases and NASA CEA are very similar. The relative error for case 2 is smaller than case 1 which makes sense since they are using the same coefficients to obtain the thermodynamic properties. The post-combustion temperature calculated by NASA CEA for the equivalence ratios calculated that yield 3383K is tabulated below in Table 7.

Case	ϕ_1	ϕ_2	T_{ϕ_1}	T_{ϕ_2}
Case 1	0.89	1.17	3377.8	3377.5
Case 2	0.92	1.4	3383	3383

Table 7: Equivalence Ratios which yield 3383K

Again we see that the results for both cases are very close, less than 1 percents relative error. However, the results from case 2 match those from NASA CEA exactly. The species mass fractions for the same equivalence points is tabulated below with the results from NASA CEA in Tables 8 and 9.

	Case 2		CEA		Relative Error	
	Phi 1	Phi 2	Phi 1	Phi 2	Phi 1	Phi 2
H2O	69.5%	80.0%	69.2%	79.7%	0%	0%
OH	12.3%	10.3%	12.9%	10.9%	5%	5%
O2	13.7%	4.5%	13.3%	4.3%	-3%	-4%
H2	1.3%	2.8%	1.3%	2.8%	-1%	0%
O	2.9%	1.8%	2.9%	1.8%	-3%	-4%
H	0.3%	0.5%	0.3%	0.4%	-1%	-1%
HO2	0.03%	0.01%	0.03%	0.01%	3%	29%

Table 8: Post-combustion Species Mass Fraction Comparison with CEA for Case 1

	Case 2		CEA		Relative Error	
	Phi 1	Phi 2	Phi 1	Phi 2	Phi 1	Phi 2
H2O	70.5%	78.7%	70.5%	78.7%	0%	0%
OH	12.9%	11.3%	12.9%	11.3%	0%	0%
O2	12.0%	5.0%	12.0%	5.0%	0%	0%
H2	1.4%	2.6%	1.4%	2.6%	0%	0%
O	2.8%	1.9%	2.8%	1.9%	0%	0%
H	0.3%	0.4%	0.3%	0.4%	-1%	0%
HO2	0.03%	0.02%	0.029%	0.015%	-3%	-33%

Table 9: Post-combustion Species Mass Fraction Comparison with CEA for Case 2

Except for HO2 which is the species with the lowest mass fraction the results of both cases are very close to the results from CEA. The results from CASE 2 are identical to those from NASA CEA except for H and HO2 which both have very low mass fractions.

6   Conclusion

The results from both case are very similar to each other with less than few percent relative error to each other for all reported values. Both cases also show good agreement with the results from NASA CEA with one exception all reported values have a relative error less

than 5%. The results from case 2 were consistently closer to those from CEA which is as expected since they are using the same coefficients to obtain the thermodynamic properties. The equivalence ratios which yielded an equilibrium temperature of 3383K were calculated to be 0.89 for the oxidizer rich mixture and 1.17 for the fuel rich mixture. In its current state the program can only handle the combustion of hydrocarbons and processes where the pressure is kept constant. Which limits its usage to rocket engines that have constant chamber pressure such as pump driven liquid and hybrid engines. Since condensed phase cannot be considered by the program hybrid engines doped with metal powders would have to assume that the metals exit as gasses.

References

[1] Jason Etele. *Fundamentals of Transatmospheric and Space Propulsion*. The Aldanox Group Inc., Dec. 2020.

[2] Sanford Gordon and Bonnie J. McBride. *Computer program for calculation of complex chemical equilibrium compositions and applications. Part 1: Analysis*. NTRS - NASA Technical Reports Server, Oct. 1994. URL: https://ntrs.nasa.gov/citations/19950013764 (visited on 03/10/2025).

[3] Mark Leader. *CEARUN rev4*. Nasa.gov, 2023. URL: https://cearun.grc.nasa.gov/cgi-bin/CEARUN/donecea3.cgi (visited on 03/13/2025).

[4] Mark Leader. *NASA Thermo Build (beta)*. cearun.grc.nasa.gov, Dec. 2023. URL: https://cearun.grc.nasa.gov/ThermoBuild/ (visited on 03/10/2025).

[5] Bonnie J. McBride, Michael J. Zehe, and Sanford Gordon. *NASA Glenn Coefficients for Calculating Thermodynamic Properties of Individual Species*. NTRS - NASA Technical Reports Server, Sept. 2022. URL: https://ntrs.nasa.gov/citations/20020085330 (visited on 03/10/2025).