An Original Method for Computing Complex Non-Premixed Flows in Chemical Equilibrium

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An Original Method for Computing Complex Non-Premixed Flows in Chemical Equilibrium

By

Raphael Cioffi

A Thesis submitted to the Graduate Studies Office in Partial Fulfillment of the Requirements for the Degree of Master of Science in Aerospace Engineering

Embry-Riddle Aeronautical University

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An Original Method for Computing Complex Non-Premixed Flows in Chemical Equilibrium

By Raphael Cioffi

This thesis was prepared under the direction of the candidate’s thesis committee chair, Dr. Eric Royce Perrell, Department of Aerospace Engineering, and has been approved by the members of this committee. It was submitted to the Graduate Studies Office and accepted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Aerospace Engineering.

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Abstract

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A novel method for computing chemical equilibrium reactions in three-dimensional reacting fluid flows is introduced in this paper. The originality of the method is that continuity equations are solved for the atomic densities rather than for the molecular species densities, as is the case for non-equilibrium flow calculations. The method is suited for applications to mixing flows in rocket engine combustors, where, due to the typical low convective speed, chemical reaction is best modeled as an equilibrium process. Equilibrium formulations usually describe the flow as a perfect, atomically uniform mix between the fuel and the oxidizer. This assumption tends to overpredict performance. Solving for the atomic densities permits the assumption of a flow in chemical equilibrium, and still allows for the spatial and temporal resolution of the molecular composition, pressure and temperature of the mixture. Properly accounting for the physical configuration of a rocket combustor, particularly the presence of separate fuel and oxidizer injectors, requires that the flow be treated as non-premixed. In this way, overall performance, and combustion instabilities, can be more accurately predicted. Transport phenomena due to molecular motion such as diffusion of the elemental masses, viscosity and conductivity are also considered, and their properties are modeled with the Chapman-Enskog theory. This study developed successively the equilibrium constants approach and the minimizations of Gibbs and Helmholtz free energies. Minimization of Helmholtz free energy was found to be the most appropriate method for Computational Fluid Dynamics (C.F.D.) implementation. In future works, we will implement this method to run test cases in parallel on the university cluster for the structured grid of a combustion chamber and exhaust nozzle of a rocket designed by the class of the thesis advisor.
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1 Introduction

1.1 Problem Statement

While assessing the performance of rocket engines, key criteria in the design such as thrust and specific impulse depend not only on the propellant used, its chemical composition and mixture ratio, but also on the location of the injectors used to distribute the fuel and oxidizer in the combustion chamber. Theoretical formulas and typical Computational Fluid Dynamics (C.F.D.) commercial software necessarily make assumptions regarding the mixing and the combustion of the reactants. The low convective speed in rocket combustion chambers favors the assumption of chemical equilibrium. Usual methods to calculate chemical equilibrium assume a perfectly pre-mixed flow and therefore neglect the importance of the injectors’ locations and the mixing of fuel and oxidizer by diffusion and convection. Relaxing the pre-mixed flow assumption by conserving molecular species separately would violate the equilibrium assumption. That is, the composition cannot be determined as both a set of conserved variables, and state variables. Molecular species can be conserved individually if non-equilibrium reactions are assumed. However, this approach requires extremely small time steps to be taken in time-accurate calculations. A method is sought whereby the chemical equilibrium assumption can be maintained, while allowing for mixing of atomically dissimilar gases. Such flows can be described as being in a state of "diffusion-limited equilibrium".
1.2 Background Research and Results

The literature on equilibrium chemical reactions is extensive and the science is fairly mature [4] [5] [15] [16]. A NASA team led by Zeleznik explored three different approaches to calculate chemical equilibrium reactions [1]. In addition, Gordon and McBride wrote a Fortran 77 computer code to determine the equilibrium composition of gas mixtures for various thermodynamic functions, the composition of the fuel and oxidizer being given whether as molecular or atomic species. This computer program, developed for the calculation of Complex Equilibrium Applications (C.E.A.) [2] [3], also calculates the performance of “quasi one-dimensional” rocket engines and considers possible shock waves and Chapman-Jouguet detonations. Camberos and Grant Moubry used yet another approach, the method of potentials, similar to the one used in this paper, to calculate the chemical composition of gases in chemical equilibrium [7]. Harlé et al. developed non-equilibrium methods [10] and applied a finite volume/element approach for an unstructured grid of a rocket engine for high speed reacting flows. Cheng, Anderson and Farmer [8] also used the non-equilibrium assumption and were therefore able to model a representative geometry with a non-premixed flow. In summary, work to date falls into one of two categories: premixed flows in equilibrium, or non-premixed flows in non-equilibrium.
1.3 **Objectives and Approach of the Research**

This thesis develops a new method to calculate chemical equilibrium reactions in a rocket engine by formulating the continuity equations with the atomic species densities, rather than the mixture density, as is usually the case in equilibrium calculations, and rather than the molecular species densities, as is usually done in non-equilibrium formulations. The molecular composition, and the other state variables, temperature and pressure, will be calculated from the solution of the Navier-Stokes equations – the atomic densities from the continuity equations, and the internal energy from the energy equation. Chemical potentials and equilibrium constants tabulated as functions of temperature will be used as inputs to the computer program. In the recast mass conservation equations, the convective and diffusive (viscous) fluxes of atomic mass are easily constructed from their molecular counterparts. In a first part, we will review the fundamentals of thermodynamics, the Navier-Stokes equations, and the different methods to model chemical equilibrium. We describe the computer subroutines using those various methods in a second part. We discuss in a third part the results obtained for the chemistry subroutines. We introduce the planned rocket test case for future calculations conducted in parallel in a fourth part. Conclusions for this project are then presented as well as recommendations for future developments and studies on this topic.
2 Theory and Governing Equations

This section summarizes the fundamental notions used for this project in thermodynamics, chemistry and aerodynamics. It also presents the basics and conditions for chemical equilibrium and three approaches to calculate it: the equilibrium constants method, and the minimizations of Gibbs and Helmholtz energies. The Navier-Stokes equations governing viscous flows, transport phenomena and properties are also detailed as well as the vector formulation of the equations for the finite volume method.

2.1 Thermodynamics Review

Propulsion is created by the conversion to kinetic energy of thermal energy released by the combustion of propellants. This review covers the basic concepts of thermodynamics, chemistry, state variables and formulations used in this project, as applied to a closed system at constant volume representing a cell of a computational grid.
2.1.1 Basic Concepts

2.1.1.1 Equation of State

For a closed system of known material at a volume $V$ and temperature $T$, there is one set of chemical species concentrations $n_i$ for which the system is at equilibrium: $n_i = n_i(V, T)$. Dalton's law for perfect gases applied to a mixture of thermally perfect gases in chemical equilibrium rewrites this relation as:

$$ p = \frac{1}{V} R_u n_{TOTAL} $$

(2.1)

where:

- $p$ = mixture pressure (Pa)
- $V$ = volume of the mixture (m$^3$)
- $T$ = temperature of the mixture (K)
- $n_{TOTAL} = $ total number of moles of the mixture (kg.mol): $n_{TOTAL} = \sum_{i=1}^{ns} n_i$
- $R_u$ = universal gas constant $R_u = 8314.3$ J/(kg.mol)
- $ns$ = number of molecular species existing in the mixture

2.1.1.2 Partial Pressure

In a mixture composed of various gases, $p_i$ is defined as the mixture pressure multiplied by the mole fraction $X_i$ of the $i^{th}$ species.

$$ p_i = pX_i $$

with: $X_i = \frac{n_i}{n_{TOTAL}}$

(2.2.a)
Partial pressures for each of the species also follow Dalton’s law for perfect gases:

\[ p_j = \frac{1}{V} R_a T n_i \]  \hspace{1cm} (2.2.b)

### 2.1.1.3 Conservation of Atomic Species

Reactants undergo a chemical transformation leading to the formation of products. The total quantity of each atomic element is constant in both sides of the equation. We must enforce this constraint in our program to represent physically the chemical reaction occurring at chemical equilibrium.

### 2.1.2 Thermodynamic Laws

#### 2.1.2.1 First Law

The first law of thermodynamics [22] states the existence of an extensive property (which is one that increases in proportion to the size of the system) called the stored energy \( E \) defined as the summation of the internal, kinetic and potential energies.

\[ E = U + KE + PE \]  \hspace{1cm} (2.3)

Where

- the internal energy \( U \) represents the energy at a molecular level of the system, due to thermal, electrostatic and chemical activities
- the kinetic energy \( KE \) is caused by the displacement of the system with respect to a reference frame
- the potential energy \( PE \) represents the energy of a system placed at a certain altitude with respect to a reference frame
The first law also states that the stored energy is in relation with the heat and work involved in the process of going from a state 1 to a state 2.

\[ E_2 - E_1 = Q_{12} - W_{12} \]  \hspace{1cm} (2.4)

Where

- \( E_2 - E_1 \) represents the change of stored energy between states 1 and 2
- \( Q_{12} \) represents the amount of heat added to the system
- \( W_{12} \) represents the work done by the system

In the energy equation, the heat added to a system and the work done by the system have a positive sign. Unlike the stored energy, which is a thermodynamic property, heat and work are path-dependent functions, and the differential form of equation (2.4) is

\[ dE = \delta Q - \delta W \]  \hspace{1cm} (2.5)

In our case, we will only consider the work of pressure, and \( \delta W = -pdV \), so that equation (2.5) becomes

\[ \delta Q = dE + pdV \]  \hspace{1cm} (2.6)

2.1.2.2 Second Law

The second law of thermodynamics postulates [22] the existence of a state function, an extensive property, called the entropy \( S \). For a closed system, entropy follows the inequality

\[ dS \geq \frac{\delta Q}{T} \]  \hspace{1cm} (2.7.a)

We consider heat transfer phenomena during the discussion of the Navier-Stokes equations in part (2.2) for a closed system enclosed in a constant volume. Energy is then solved as a conserved variable and we can consider our system to be adiabatic for the derivations of the
thermodynamic equations, thus $\delta Q = 0$, and the second law of thermodynamics can be expressed as:

$$dS \geq 0$$

Hence, any change occurring in our system tends to increase its entropy. When the system has finished undergoing a transformation, it reaches equilibrium. The entropy is then a constant and $dS = 0$, meaning that entropy has reached a maximum value. Chemical equilibrium can then be formulated by maximizing the entropy function.

### 2.1.3 State Variables

This part presents the expression of various state variables: the internal energy, Gibbs free energy and Helmholtz free energy.

#### 2.1.3.1 Internal Energy

If we consider that no change in kinetic or potential energies occurs in our closed system for the derivation of the state variables, and we can rewrite the first law of thermodynamics (2.3) as

$$dE = dU + dKE + dPE$$

$$dE = dU$$

so that: $\delta Q = dU + pdV$, and for our adiabatic case: $dU = -pdV$ \hspace{1cm} (2.8)
2.1.3.2 Gibbs Free Energy

From the first law of thermodynamics (2.8), \( dU + pdV = \delta Q \), and from the second law of thermodynamics (2.7.a), \( \delta Q \leq TdS \), we get

\[
dU + pdV - TdS \leq 0 \quad (2.9.a)
\]

Considering a constant pressure and constant temperature process,

\[
d(U + pV - TS)_{p,T} \leq 0 \quad (2.9.b)
\]

where the subscripts denote the variables held constant. One can define the Gibbs function or Gibbs free energy as

\[
G = U + pV - TS \quad (2.9.c)
\]

We express the second law of thermodynamics with equation (2.9.b) as

\[
d(G)_{p,T} \leq 0 \quad (2.9.d)
\]

Thus, any change to our closed system tends to decrease the Gibbs energy. When a system has finished undergoing a transformation and reaches equilibrium, \( d(G)_{p,T} = 0 \), meaning that the Gibbs function is at a minimum. Therefore, another possible method for obtaining chemical equilibrium is to minimize Gibbs energy.

Differentiating equation (2.9.c), we get

\[
dG = dU + pdV + VdP - TdS - SdT \quad (2.10)
\]

Substituting equation (2.9.a), we get the inequality

\[
dG \leq Vdp - SdT \quad (2.11.a)
\]

For an isothermal process,

\[
(dG)_T \leq Vdp \quad (2.11.b)
\]
which also represents the second law of thermodynamics, so when the process has reached equilibrium,

\[ dG = Vdp \]  

(2.11.c)

Substituting Dalton's second law,

\[ (dG)_T = nR_u T \frac{dp}{p} \]  

(2.12.a)

\[ (dG)_T = nR_u T d[\ln(p)] \]

Integrating this relation from standard state to present condition

\[ G = G^0 + nR_u T \ln \left( \frac{p}{p_0} \right) \]  

(2.12.b)

In the former expression, \( p \) and \( p_0 \) have units of bars. If \( p_0 \) is equal to one bar (10^5 Pa), we can rewrite the formula (2.12.b)

- For the whole mixture:
  \[ G = G^0 + n_{\text{TOTAL}} R_u T \ln \left( \frac{p}{p_0} \right) \]  
  (2.13.a)

- For each one of the species
  \[ G_i = G_i^0 + n_i R_u T \ln \left( \frac{p_i}{p} \right) \]  
  (2.13.b)

Values for \( G_i^0 \) as a function of temperature can be found in JANAF Thermochemical Tables [11]. For a closed system at constant temperature and constant pressure in chemical equilibrium, the Gibbs energy is a minimum.

The minimization of the thermodynamic function \( G \) is also subject to the atomic species mass constraint. Therefore we define a Lagrangian \( L \), which is a function of the unknown species number of moles \( n_i \), and the Lagrange multipliers \( \lambda_j \), where \( j \) represents the atomic species present in the reaction, namely in our case, H, C or O.
The Lagrangian $L$ is

$$L = \sum_{i=1}^{\text{ns}} \left( G_i^0 + R_u T \ln \left( \frac{P n_i}{n} \right) \right) n_i + \sum_{j=H,C,O} \lambda_j \left( \sum_{i=1}^{\text{ns}} a_{ij} n_i - b_j^0 \right)$$

(2.14)

in which

- subscript $i$ refers to the molecular species, from 1 to ns (Number of species),
- subscript $j$ refers to one of the atomic species present in our reaction, H, C or O,
- $T$ is the temperature of the mixture,
- $G_i^0$ is the Gibbs energy at the temperature $T$, in J/(kg.K)
- $R_u$ is the fundamental gas constant equal to 8314.51 J/(kg.mol)(K),
- $P$ is the mixture pressure in bars,
- $n_i$ is the total number of moles in (kg.mol) of species $i$,
- $n$ is the total number of moles in (kg.mol) of the mixture,
- $\lambda_j$ is the Lagrange multiplier to be solved for each of the atomic species,
- $a_{ij}$ are the stoichiometric coefficients stating how many number of kg.mol of atomic species $j$ is included into species $i$. Example, for $n_3 = n_{\text{H}_2\text{O}}$, if $j=1$ corresponds to H and $j=2$ corresponds to O, then $a_{31}=2$ and $a_{32}=1$
- $b_j^0$ corresponds to the total number of moles of atomic species $j$ in the reaction.

In order to find the minimum of the Lagrangian, we differentiate equation (2.14) with respect to all the unknowns in turn, keeping all the other ones constant, and setting each one of these derivatives equal to zero.
Assuming that the total number of moles is constant throughout the whole process, we have the following system of nonlinear equations:

\[
\frac{\partial (L)}{\partial n_i} = G_i^0 + R_a T \left( \ln \left( \frac{P n_i}{n} \right) + 1 \right) + \sum_{j=H,C,O} \left( \lambda_j, \sum_{i=1}^{n_i} a_j \right) = 0, i = 1, \ldots, n_s
\]

The second set of equations represents the atomic species mass balance. This set of new equations must be solved simultaneously.

Another approach is to consider the total number of moles as a variable, since in the process of solving the system, species numbers of moles vary. The differentiations of the set of Lagrangians changes slightly:

\[
\frac{\partial (L)}{\partial n_i} = G_i^0 + R_a T \left( \ln \left( \frac{P n_i}{n} \right) + 1 - \frac{\sum_{j=1}^{n_s} n_j}{n} \right) + \sum_{j=H,C,O} \left( \lambda_j, \sum_{i=1}^{n_i} a_j \right) = 0, i = 1, \ldots, n_s
\]

Since these equations are not linear, we use an iterative process to find the solution of the system. The Newton-Raphson method used to iteratively solve the system \( S \) of equations is explained in Part 3.2.4. and the implementation of the algorithm is furthermore detailed in Part 3.5.2.
2.1.3.3 Helmholtz Free Energy

From equation (2.9.a),
\[ dU + pdV - TdS \leq 0 \]

And for a constant volume,
\[ dU - TdS \leq 0. \] (2.17.a)

If we also consider a constant temperature, then
\[ d(U - TS) \leq 0 \] (2.17.b)

One can define the Helmholtz function or Helmholtz Free Energy as
\[ F = U - TS \] (2.18.a)

which is equivalent to
\[ F = G - pV \]

Hence, equation (2.17.b) represents the second law of thermodynamics
\[ (dF)_{v,T} \leq 0 \] (2.18.b)

Thus, any change to our closed system tends to decrease the Helmholtz energy. When a system has finished undergoing a transformation and reaches equilibrium, \( d(F)_{v,T} = 0 \), meaning that the Helmholtz function is at a minimum. Therefore, another possible method for obtaining chemical equilibrium is to minimize the Helmholtz energy.

As said before, \( F = G - pV \), thus:
\[ F = G^0 + n_{TOTAL} R_u T \ln \left( \frac{P}{P_0} \right) - pV \] (2.19)
From equations (2.13.a) and (2.13.b), we find similar formulas for the Helmholtz free energy. When substituting the pressure using Dalton’s law for perfect gas and assuming $p_0 = 1$ bar ($10^5$ Pa), we get

- For the whole mixture:
  \[ F = G^0 + n_{\text{TOTAL}} R_u T \ln \left( \frac{n_{\text{TOTAL}} R_u T}{10^5 V} \right) - n_{\text{TOTAL}} R_u T \]  
  (2.20.a)

- For each species:
  \[ F_i = G^0_i + n_i R_v T \ln \left( \frac{n_i R_v T}{10^5 V} \right) - n_i R_v T \]  
  (2.20.b)

For a closed system at constant volume and constant temperature, we can minimize Helmholtz energy as a function of the temperature only, in order to achieve chemical equilibrium. Since the minimization of Helmholtz free energy is also subjected to the atomic mass constraint, we use another Lagrangian $L$ and Lagrange multipliers. The trick is to substitute the mixture pressure $P$ in the equations by the volume $V$ using Dalton’s law of perfect gases.

For a constant number of moles, $L$ becomes:

\[ L = \sum_{i=1}^{n_s} \left( G^0_i + R_u T \ln \left( \frac{n_i R_u T}{10^5 V} \right) \right) n_i - PV + \sum_j \lambda_j \left( \sum_{i=1}^{n_s} a_{ij} n_i - b_j^0 \right) \]  
(2.21)

In order to find the condition for equilibrium, we solve the following system, assuming that the total number of moles $n$ changes:

\[ \frac{\partial(L)}{\partial n_i} = G^0_i + R_u T \ln \left( \frac{n_i R_T}{10^5 V} \right) + \sum_{j=H,C,O} \lambda_j \sum_{i=1}^{n_s} a_{ij} n_i = 0, i = 1, \ldots, n_s \]  

\[ \frac{\partial(L)}{\partial \lambda_j} = \left( \sum_{i=1}^{n_s} a_{ij} n_i \right) - b_j^0 = 0, j = H, C, O \]  
(2.22)
We use once again the Newton-Raphson iterative process to solve simultaneously the non-linear equations of this system. This approach is very useful when both the temperature and the volume are constant at every step of the iteration. The constant volume assumption is appropriate for application to each computational cell of known volume in the CFD calculations. Later it will be shown how the constant temperature assumption can be relaxed by including the definition of total energy, a conserved variable, in the equation set. Details are in Part 3.5.3.

2.1.4 Equilibrium Constants

The method to determine the molecular composition of a mixture in chemical equilibrium by using the equilibrium constants was the first one to be developed [4] [5]. Consider a simple reactive mixture written in the stoichiometric form as:

$$n_1 C_1 + n_2 C_2 \rightarrow n_3 C_3 + n_4 C_4$$

where

- $n_1$ and $n_2$ are the quantities (in kg.mol) of reactants $C_1$ and $C_2$
- $n_3$ and $n_4$ are the quantities of products $C_3$ and $C_4$ formed in the reaction.

If we assume $p_0 = 1$ bar and apply equation (2.13.b) to each of the species in the mixture, we can find the Gibbs functions for each species of the system as

$$G_{C_i} = G_{C_i}^0 + n_i R_u T \ln \left( \frac{p_{C_i}}{P_i} \right)$$

(2.23)
The difference in Gibbs free energy occurring during the reaction is given by

\[
\Delta G = G_{\text{products}} - G_{\text{reactants}}
\]

\[
\Delta G = (G_1 + G_2) - (G_1 + G_2)
\]

\[
\Delta G = (G^0_1 + G^0_2) - (G^0_1 + G^0_2)
\]

\[+ R_u T \left( n_3 \ln p_{C_1} + n_4 \ln p_{C_2} - n_4 \ln p_{C_1} - n_2 \ln p_{C_2} \right)
\]

\[
\Delta G = \Delta G^0 + R_u T \ln \left( \frac{p_{C_1}^{n_3} p_{C_2}^{n_4}}{p_{C_1}^{n_4} p_{C_2}^{n_2}} \right)
\]

At equilibrium, \( d(G)_p = 0 \), then \( \Delta G = 0 \), for particular values of temperature and pressure,

and \( -\Delta G^0 = R_u T \ln \left( \frac{p_{C_1}^{n_3} p_{C_2}^{n_4}}{p_{C_1}^{n_4} p_{C_2}^{n_2}} \right) \) \hspace{1cm} (2.25)

We define the equilibrium constant \( K_p \) for the reaction as

\[
K_p = \left( \frac{p_{C_1}^{n_3} p_{C_2}^{n_4}}{p_{C_1}^{n_4} p_{C_2}^{n_2}} \right)
\]

so that \( -\Delta G^0 = R_u T \ln \left( K_p \right) \).

From the definition of partial pressure, an alternate equation for the equilibrium constant is

\[
K_p = \left( \frac{n_3^{n_3} n_4^{n_4}}{n_1^{n_4} n_2^{n_2}} \right) \left( \frac{P_{\text{MIXTURE}}}{n_{\text{TOTAL}}} \right)^{n_3+n_4-(n_1+n_2)}
\]

\hspace{1cm} (2.26.b)

From equation (2.26.b), it is noticeable that \( K_p \) has units of pressure \( p \) elevated to the power \( \left( \sum_{\text{products}} n_i - \sum_{\text{reactants}} n_i \right) \). Decimal logarithms of the equilibrium constants are tabulated in the JANAF Thermochemical Tables [11] as a function of temperature at a given reference pressure of one bar. At a given temperature and pressure, there exists only one composition of the mixture, in terms of molecular species concentrations, based on the equilibrium constants. This method, even though leading to highly non-linear equations, seemed attractive at the beginning of the project for its very simple formulation. Results and comments are later explained in Part 3.5.1.
2.1.5 Heat of Formation and Heat of Reaction

Heat of reaction and heat of formation are energies associated with the chemical reactions and transformations involved in a chemical process. They are used in the calculation of the internal energy in the Navier-Stokes equations presented in Part 2.2.

2.1.5.1 Heat of Formation

The standard heat of formation $\Delta H_f^0$ is defined as the quantity of heat involved when one mole of substance is formed from its elements in their respective standard states at the standard conditions of 298.15 K and 1 bar of pressure. The heat of formation of an element already in its reference (or standard) state is zero by definition. Values for species in an alternate state can be found in various tables such as the JANAF Thermochemical Tables [11]. They can also be calculated from the bond energies, which are energies that a particular bond between two atomic species has, such as the C=H or O-H bonds for example. The following examples explain this concept.

\[ C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} -94.054 \text{kcal/mol} \]

where -94.054 kcal/mol is $(\Delta H_f^0)_{CO_2}$ at 298.15 K. Since this quantity is negative, that means that the reaction is exothermic.

\[ H_{2(g)} \rightarrow 2H_{(g)} +104.2 \text{kcal} \]

where 104.2 kcal represents twice the amount $(\Delta H_f^0)_H = 52.1 \text{ kcal/mol}$. Since this quantity is positive, the reaction is said to be endothermic, because heat is needed in order for the process to take place.
2.1.5.2 Heat of Reaction

When a chemical reaction takes place, there is a change of heat associated with it. When the change is being carried out in a random process, this quantity is indefinite, because it depends on the thermodynamic path taken. It is however possible to define this heat only by its initial and final states when the process is at constant pressure or constant volume. Our derivation follows that of Kuo [5]

![Diagram](image.png)

**Figure 1: Two Temperature-Reaction Paths**

(From Kuo [5])

From equations (2.8), we can write the first law as

\[ \Delta^2 U = Q_{12} - W_{12} \]  

(2.27)

If moreover the reaction occurs at constant pressure, we have:

\[ Q_p = \int (\delta Q)_p = \Delta U + p \Delta V \]  

(2.28)

Between two states A and B this equation becomes

\[ Q_p = (U_B - U_A) + p(V_B - V_A) \]  

\[ Q_p = (U_B + pV_B) - (U_A + pV_A) \]  

(2.29)

\[ Q_p = H_B - H_A = \Delta H \]
We can prove the same way that at constant volume \( Q_v = \Delta H \). From Dalton’s law for perfect gases, and using the above result for a reaction at constant temperature:

\[
\Delta H_{r,T} = \Delta U + p\Delta V \\
p\Delta V = (\Delta n) R_u T \\
\Delta H_{r,T} = \Delta U + (\Delta n) R_u T
\]  

(2.30)

where: \( \Delta n = \left[ \left( \sum_{i=1}^{N} n_i \right)_{\text{products}} - \left( \sum_{i=1}^{N} n_i \right)_{\text{reactants}} \right]_{\text{gaseous species}} \)

From Figure 1, we have the following relations

\[
(\text{heat change})_{\text{path A}} = (\text{heat change})_{\text{path B}} \]

\[
\Delta H_{\text{reactants}} + \Delta H_{r,T_1} = \Delta H_{r,T_2} + \Delta H_{\text{products}} \\
\Delta H_{\text{reactants}} = \sum_{i=1}^{N} (n_i,\text{reactants}) \int_{T_1}^{T_2} C_{p,i} dT \\
\Delta H_{\text{products}} = \sum_{i=1}^{N} (n_i,\text{products}) \int_{T_1}^{T_2} C_{p,i} dT
\]  

(2.31)

where \( C_p \)'s are the constant-pressure specific heats, and are found from tables such as [11] [13], for example.

The heat of reaction at standard state \( \Delta H_{r,T_0} \) at \( T_0 \) is related to the heat of formation in the following way:

\[
\Delta H_{r,T_0} = \sum_{i=1}^{\gamma} \nu_i \Delta H_{f,T_0}^{\text{reactants}} - \sum_{i=1}^{\gamma} \nu_i \Delta H_{f,T_0}^{\text{products}}
\]  

(2.32)

where \( \nu_i \) reacting moles of atomic elements \( M_i \) produce \( \nu_i' \) moles of atomic elements \( M_i' \), each of which have the heat of formation \( \Delta H_{f,M_i}^{0} \). We used these relations in order to calculate the internal energy of a given cell of our volume while solving the Navier-Stokes equations presented in the following part.
2.2 *Navier-Stokes Equations*

The Navier-Stokes equations are expressions of the conservation of mass, of linear momentum, and of energy. In this study, we consider a non-premixed, viscous, laminar, three-dimensional mixture flow.

2.2.1 *Conservation of Mass*

The equation representing the conservation of mass, also known as the continuity equation, states that no mass in a closed system is lost during the process. This principle can be expressed in the following forms, for a mixture of mass $m$ contained in a volume $V$ of surface area orthogonal vector $d\vec{A}$, at a speed $\vec{V}$:

- In an integral form: $\frac{Dm}{Dt} = \frac{\partial}{\partial t} \int_V \rho dV + \int_A \rho \vec{V} \cdot d\vec{A} = 0$ (2.33.a)
- In a differential form: $\frac{\partial \rho}{\partial t} + (\nabla \cdot \rho \vec{V}) = 0$ (2.33.b)
- In a Cartesian system: $\frac{\partial \rho}{\partial t} + \frac{\partial (\rho u)}{\partial x} + \frac{\partial (\rho v)}{\partial y} + \frac{\partial (\rho w)}{\partial z} = 0$ (2.33.c)
2.2.2 Conservation of Linear Momentum

The conservation of linear momentum is derived from Newton's second law of motion:

\[
\sum \overrightarrow{F}_{\text{external}} = \frac{D(\text{Momentum})}{Dt} = \frac{\partial}{\partial t} \left( \int \overrightarrow{V} \rho d\mathbf{V} \right) + \int \overrightarrow{V} (\rho \overrightarrow{v} \cdot d\mathbf{A}) = \overrightarrow{F}_{\text{external}} + \overrightarrow{F}_{\text{body}} - \int \rho d\mathbf{A} \quad (2.34.a)
\]

External forces are comprised of body forces, pressure forces, and viscous forces. The vector equation above is projected to the three axes of the Cartesian reference frame to produce three algebraic equations.

- X-axis:
  \[
  \frac{\partial}{\partial t} \left( \rho u \right) + \frac{\partial}{\partial x} \left( \rho uu + P - \tau_{xx} \right) + \frac{\partial}{\partial y} \left( \rho vu - \tau_{xy} \right) + \frac{\partial}{\partial z} \left( \rho wu - \tau_{xz} \right) = \rho X \quad (2.34.b)
  \]

- Y-axis:
  \[
  \frac{\partial}{\partial t} \left( \rho v \right) + \frac{\partial}{\partial x} \left( \rho uv + P - \tau_{yy} \right) + \frac{\partial}{\partial y} \left( \rho vv + P - \tau_{yy} \right) + \frac{\partial}{\partial z} \left( \rho wv - \tau_{yz} \right) = \rho Y \quad (2.34.c)
  \]

- Z-axis:
  \[
  \frac{\partial}{\partial t} \left( \rho w \right) + \frac{\partial}{\partial x} \left( \rho uw - \tau_{xz} \right) + \frac{\partial}{\partial y} \left( \rho vw - \tau_{yz} \right) + \frac{\partial}{\partial z} \left( \rho wv + P - \tau_{zz} \right) = \rho Z \quad (2.34.d)
  \]

where \( X, Y \) and \( Z \) are the components of the body forces, and the viscous tensor terms \( \tau \) are defined as:

\[
\tau_{xx} = \frac{2}{3} \mu \left( 2 \frac{\partial u}{\partial x} - \frac{\partial v}{\partial y} - \frac{\partial w}{\partial z} \right)
\]

\[
\tau_{yy} = \frac{2}{3} \mu \left( 2 \frac{\partial v}{\partial y} - \frac{\partial u}{\partial x} - \frac{\partial w}{\partial z} \right)
\]

\[
\tau_{zz} = \frac{2}{3} \mu \left( 2 \frac{\partial w}{\partial z} - \frac{\partial u}{\partial x} - \frac{\partial v}{\partial y} \right)
\]

\[
\tau_{xy} = \tau_{yx} = \mu \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right)
\]

\[
\tau_{xz} = \tau_{zx} = \mu \left( \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right)
\]

\[
\tau_{yz} = \tau_{zy} = \mu \left( \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y} \right)
\]

\[
(2.35)
\]
2.2.3 Conservation of Energy

The conservation of energy makes use of the first law of thermodynamics (equation 2.5)

\[
\frac{\partial}{\partial t} \int \rho dV + \int e \left( \rho \bar{V} d\bar{A} \right) = \frac{\delta Q}{\delta t} + \frac{\delta W}{\delta t} \tag{2.36.a}
\]

which, after having applied the divergence theorem for a differential size control volume, leads to:

\[
\frac{\partial (\rho e)}{\partial t} + \nabla \left( \rho \bar{V} \right) = \left( \frac{\delta Q}{dV} \right) + \left( \frac{\delta W}{dV} \right) \tag{2.36.b}
\]

In the Cartesian reference frame, equation (2.36.b) becomes:

\[
\frac{\partial (\rho e)}{\partial t} + \frac{\partial}{\partial x} \left( \rho u e + uP - u\tau_{xx} - \nu \tau_{xy} - w\tau_{xz} + q_x \right) + \frac{\partial}{\partial y} \left( \rho v e + vP - u\tau_{yx} - \nu \tau_{yy} - w\tau_{yz} + q_y \right) + \frac{\partial}{\partial z} \left( \rho w e + wP - u\tau_{xz} - \nu \tau_{yz} - w\tau_{zz} + q_z \right) = \rho q + \rho (uX + vY + wZ) \tag{2.36.c}
\]

2.2.4 Transport Properties for the Viscous Fluxes

The viscous fluxes are key to the process we wish to model. Viscous fluxes are those that occur as a result of gradients in molecular species mass concentrations, velocities, and temperatures. Large gradients occur at the interface between the propellant streams and the reacting mixture, between localized regions with differing properties, and between large turbulent eddies. We assume that reactions occur infinitely fast in comparison to the rate at which fuel and oxidizer mix. Mixing at the molecular level is mass diffusion, the rate of which is influenced by macroscopic mixing as shear regions “roll up” into eddies.
The viscous fluxes are mass diffusion, shear stress, and thermal conduction. The fluxes are proportional to the magnitudes of gradients in the transported variables. The proportionality constants are properties of the gas mixture: diffusion coefficient, viscosity, and thermal conductivity, respectively. Approximations to these transport properties are made as functions of temperature according to the Chapman-Enskog equations.

### 2.2.4.1 Newton's Law of Viscosity

The Chapman-Enskog theory gives an expression for the transport of momentum in terms of a potential energy of attraction between two molecules in the gas. The dynamic viscosity for each gas at low density composing the mixture is a function of the temperature and is calculated by the formula

\[ \mu = 2.6693 \times 10^{-5} \frac{\sqrt{MT}}{\sigma^2 \Omega_{\mu}} \]  

(2.37.a)

where \( M \) represents the molecular weight of the gas, \( \sigma \) is the first Lennard-Jones parameter, \( T \) is the temperature of the gas, and \( \Omega_{\mu} \) is the collision cross section for viscosity, and is a function of the reduced temperature \( kT/\varepsilon \) found in tables such as [14]. We then apply Wilke's semi-empirical formula to calculate the viscosity for the mixture

\[ \mu_{\text{mix}} = \sum_{i=1}^{n} \frac{x_i \mu_i}{\sum_{j=1}^{n} x_j \Phi_j} \]  

(2.37.b)

in which:

\[ \Phi_j = \frac{1}{\sqrt{8}} \left( 1 + \frac{M_i}{M_j} \right)^{-1/2} \left[ 1 + \left( \frac{\mu_i}{\mu_j} \right)^{1/2} \left( \frac{M_j}{M_i} \right)^{1/4} \right]^2 \]  

(2.37.c)
2.2.4.2 *Fourier's Law of Heat Conduction*

This law states that the heat flux vector $\vec{q}$ is proportional to the gradient of temperature $T$ and in opposite direction:

$$\vec{q} = -k \nabla T$$  \hspace{1cm} (2.38.a)

The determination of the thermal conductivity $k$ is therefore crucial to calculate the flux of heat in a gas. A theory for monatomic gases at low densities is complete, but the one for polyatomic gases is still under development. As a first approximation, we can once again assume that we are using a low-density gas mixture. We apply the Chapman-Enskog theory to calculate the thermal conductivities for monatomic gases and we use the Eucken approach for polyatomic gases.

- For a monatomic gas: $k = 1.9891 \times 10^{-4} \frac{\sqrt{T/M}}{\sigma^2 \Omega}$ \hspace{1cm} (Chapman-Enskog) \hspace{1cm} (2.38.b)
- For a polyatomic gas: $k = \left( \tilde{C}_v + \frac{5R}{4M} \right) \mu$ \hspace{1cm} (Eucken) \hspace{1cm} (2.38.c)

Note that the Eucken approach uses the dynamic viscosity term calculated in the previous section by the Chapman-Enskog method. When the thermal conductivities for each species have been calculated, whether the species is monatomic or polyatomic, the mixture thermal conductivity is then calculated by

$$k_{mix} = \sum_{i=1}^{n_i} \frac{x_i k_i}{\sum_{j=1}^{n_j} x_j \Phi_{ij}}$$  \hspace{1cm} (2.38.d)

where $\Phi_{ij}$ is given by equation (2.37.c).
2.2.4.3 Fick’s Law of Diffusion

Diffusion is the process by which materials move from one position to another because of the random motion of molecules. Since there are more molecules in areas of greater concentration, there are many more collisions between the molecules and more probability that some of them will be forced to go to an area of lower concentration. A similar process is the conduction of heat in a bar in which one end is heated while the other end is left free: a heat flux is directed from the area of high temperature to the area of lower temperature. Fick’s law accounts for this process and can be written for a system comprised of species A and B, in the following way:

\[ \mathbf{J}_A = -cD_{AB} \nabla X_A \]  

(2.39.a)

Where:

- \( \mathbf{J}_A \) = molar diffusion flux
- \( X_A \) = molar fraction of species A

\[ \nabla = \frac{\partial}{\partial x} \mathbf{i} + \frac{\partial}{\partial y} \mathbf{j} + \frac{\partial}{\partial z} \mathbf{k} \]

is the gradient vector operator

\( D_{AB} \) = diffusivity of the gas

We apply once again the kinetic theory to calculate the value of the term \( (cD_{AB}) \) for low-density gases using the Chapman-Enskog formula

\[ cD_{AB} = 2.2646 \times 10^{-5} \sqrt{\frac{T}{\sigma_{AB}^3\Omega_{D,AB}}} \]  

(2.39.b)

where \( \Omega_{D,AB} \) is the collision cross section for diffusion.

This part presented the Navier-Stokes equations along with the transport phenomena taken into account. The formulation of the Navier-Stokes equations also depends on the chemical model chosen and is presented next.
2.3 Finite Volume and Vector Formulation

The Navier-Stokes equations can be written in a vector form as follows:

\[
\frac{\partial \overline{Q}}{\partial t} + \frac{\partial \overline{E}}{\partial x} + \frac{\partial \overline{F}}{\partial y} + \frac{\partial \overline{G}}{\partial z} = 0
\]  

(2.40)

where

\[
\overline{Q} = \begin{bmatrix}
\rho_H u \\
\rho_C u \\
\rho_O u \\
\rho u + P \\
\rho u v \\
\rho u w \\
\rho (e + P) u
\end{bmatrix}
\]  

(2.41.a)

The subscripts H, C and O denote the atomic species (hydrogen, carbon, and oxygen) for which the densities are solved in the continuity equations, for the diffusion-limited approach.

We separate each of the vectors E, F and G into an inviscid and a viscous component:

\[
\overline{E}_I = \begin{bmatrix}
\rho_H u \\
\rho_C u \\
\rho_O u \\
\rho u + P \\
\rho u v \\
\rho u w \\
\rho (e + P) u
\end{bmatrix}
\]  

(2.41.b)

\[
\overline{E}_V = \begin{bmatrix}
\rho \sum_{i=1}^{n_i} a_{iH} \overline{D}_i \frac{\partial X_i}{\partial x} \frac{MW(H)}{MW(i)} \\
\rho \sum_{i=1}^{n_i} a_{iC} \overline{D}_i \frac{\partial X_i}{\partial x} \frac{MW(C)}{MW(i)} \\
\rho \sum_{i=1}^{n_i} a_{iO} \overline{D}_i \frac{\partial X_i}{\partial x} \frac{MW(O)}{MW(i)} \\
\tau_{xx} \\
\tau_{xy} \\
\tau_{xz} \\
u \tau_{xx} + \nu \tau_{xy} + \nu \tau_{xz} + k \frac{\partial T}{\partial x} + \rho \sum_{i=1}^{n_i} \overline{h}_i^0 \overline{D}_i \frac{\partial X_i}{\partial x}
\end{bmatrix}
\]  

(2.41.c)
\[
\begin{align*}
\bar{F}_f &= \begin{bmatrix}
\rho \dot{v}
\rho_c \dot{v}
\rho_o \dot{v}
\rho_{vu}
\rho_{vv} + P
\rho_{vw}
\rho (e + P) v
\end{bmatrix} \\
\bar{F}_v &= -
\begin{bmatrix}
\rho \sum_{i=1}^{\infty} a_{hi} D_i \frac{\partial X_i}{\partial y} \frac{MW(H)}{MW(i)} \\
\rho \sum_{i=1}^{\infty} a_{ci} D_i \frac{\partial X_i}{\partial y} \frac{MW(C)}{MW(i)} \\
\rho \sum_{i=1}^{\infty} a_{io} D_i \frac{\partial X_i}{\partial y} \frac{MW(O)}{MW(i)} \\
\tau_{xx} \\
\tau_{yx} \\
\tau_{yy} \\
\tau_{zx} \\
\tau_{zy} \\
\tau_{yy} \\
\end{bmatrix} \\
\bar{G}_f &= \begin{bmatrix}
\rho \dot{w}
\rho_c \dot{w}
\rho_o \dot{w}
\rho_{wu}
\rho_{ww}
\rho_{ww} - \tau_{zz}
\rho (e + P) w
\end{bmatrix} \\
\bar{G}_v &= -
\begin{bmatrix}
\rho \sum_{i=1}^{\infty} a_{hi} D_i \frac{\partial X_i}{\partial z} \frac{MW(H)}{MW(i)} \\
\rho \sum_{i=1}^{\infty} a_{ci} D_i \frac{\partial X_i}{\partial z} \frac{MW(C)}{MW(i)} \\
\rho \sum_{i=1}^{\infty} a_{io} D_i \frac{\partial X_i}{\partial z} \frac{MW(O)}{MW(i)} \\
\tau_{zx} \\
\tau_{xz} \\
\tau_{zz} \\
\tau_{zx} \\
\tau_{xz} \\
\end{bmatrix}
\end{align*}
\]
where $X_i$ represents the mass fraction of molecular species, and $\rho$ denotes the mixture density and is the summation of the densities of the three atomic elements $\rho_H$, $\rho_C$ and $\rho_O$. We write the previous equations on a per volume basis and we solve them in a vector form using a central difference scheme in space. Conversion between the body-fitted coordinate system ($\xi, \eta, \zeta$) and the Cartesian coordinate system ($x, y, z$) allows these equations to be applied to the particular grid that we will use. We can apply the chain rule in order to express the derivatives with respect to the Cartesian system with the Body-fitted system.

\[
\begin{align*}
\xi &= \xi(x, y, z) \\
\eta &= \eta(x, y, z) \\
\zeta &= \zeta(x, y, z) \\
\frac{\partial}{\partial x} &= \xi_x \frac{\partial}{\partial \xi} + \eta_x \frac{\partial}{\partial \eta} + \zeta_x \frac{\partial}{\partial \zeta} \\
\frac{\partial}{\partial y} &= \xi_y \frac{\partial}{\partial \xi} + \eta_y \frac{\partial}{\partial \eta} + \zeta_y \frac{\partial}{\partial \zeta} \\
\frac{\partial}{\partial z} &= \xi_z \frac{\partial}{\partial \xi} + \eta_z \frac{\partial}{\partial \eta} + \zeta_z \frac{\partial}{\partial \zeta} \\
\frac{\partial}{\partial \xi} &= x_x \frac{\partial}{\partial x} + y_x \frac{\partial}{\partial y} + z_x \frac{\partial}{\partial z} \\
\frac{\partial}{\partial \eta} &= x_\eta \frac{\partial}{\partial x} + y_\eta \frac{\partial}{\partial y} + z_\eta \frac{\partial}{\partial z} \\
\frac{\partial}{\partial \zeta} &= x_\zeta \frac{\partial}{\partial x} + y_\zeta \frac{\partial}{\partial y} + z_\zeta \frac{\partial}{\partial z}
\end{align*}
\]

Solving the equations for the derivatives with respect to $x$, $y$, and $z$, we find the expression of the Navier-Stokes vector equation (2.40) with respect to the body-fitted coordinate system

\[
\frac{\partial \bar{Q}}{\partial t} + \frac{\partial \bar{E}'}{\partial \xi} + \frac{\partial \bar{F}'}{\partial \eta} + \frac{\partial \bar{G}'}{\partial \zeta} = 0
\]

where:

\[
\begin{align*}
\bar{E}' &= \xi_x \bar{E} + \xi_y \bar{F} + \xi_z \bar{G} \\
\bar{F}' &= \eta_x \bar{E} + \eta_y \bar{F} + \eta_z \bar{G} \\
\bar{G}' &= \zeta_x \bar{E} + \zeta_y \bar{F} + \zeta_z \bar{G}
\end{align*}
\]
The spatial derivatives are evaluated using a finite volume scheme, based on the divergence theorem (Stokes) applied to the cell; changes in the conserved variables are expressed as a difference of fluxes through the volume. The following picture explains the concept for a two-dimensional cell.

\[ \frac{\partial \hat{E}'}{\partial \xi} + \frac{\partial \hat{F}'}{\partial \eta} = \hat{E}'_{i+\frac{1}{2},j} \cdot \vec{n}_{i+\frac{1}{2},j} + \hat{E}'_{i-\frac{1}{2},j} \cdot \vec{n}_{i-\frac{1}{2},j} + \hat{F}'_{i,j+\frac{1}{2}} \cdot \vec{n}_{i,j+\frac{1}{2}} + \hat{F}'_{i,j-\frac{1}{2}} \cdot \vec{n}_{i,j-\frac{1}{2}} \]  \hspace{1cm} (2.45)

where \( \vec{n}_{i,j} \) represents the vector normal to the face \((i,j)\). The next part presents the program used to implement the various methods to calculate the three-dimensional flow.
3 Computational Resolution of the Problem

This chapter presents a general overview of the program, some important data curve fittings, and the iterative process that we use to solve the chemical composition of the flow field. The last part presents the various chemistry subroutines implemented.

3.1 General Overview of the Program

The method was part of a C.F.D. code under development at the university’s Propulsion and Aerodynamics Computational Laboratory (P.A.C.L.). This program aims in the end at solving several types of flows, namely:

- Flows involving air in equilibrium
- Premixed flows in thermochemical equilibrium
- Non-premixed flows in thermochemical equilibrium
- Flows in chemical non-equilibrium, in vibrational and rotational equilibrium
- Flows in chemical and vibrational non-equilibrium, and in rotational equilibrium
- Flows in chemical, vibrational and rotational non-equilibrium

This thesis addresses the third problem. The following diagram explains the algorithm used in the program.
Initialization of the cluster

Input file

Arrays allocations

Store the database for each species into an array

Calculate the number of variables for the solution vector

Read the boundary conditions from a file

Read grid elements, compute cell volumes and surfaces, ghost cells, and metric derivatives

Set the interior mesh to free stream conditions, initialize the chemical composition using Gibbs free energy minimization

For a certain number of times

Calculate the time step

Message pass conserved variables along inter-processor boundaries

Compute the transport properties: mu, kappa, \(cD\)

Compute fluxes and update conserved variables

Compute chemical composition and state variables using minimization of Helmholtz free energy

Output results in a record file

END

Figure 3: Main Program Flow Chart
The input file contains the following data:

- **Free stream conditions**: velocity components, temperature, pressure
- **Iteration properties**: maximum number of iterations, maximum tolerance
- **Chemical properties**: number of species and their name (the atomic species will be found from there)
- **Code resolution**: problem to be solved, implicit or explicit scheme, two-dimensional or three-dimensional

For each of the species, the following data are stored:

- Enthalpy coefficients from 0 to 6000 K (from curve fitting)
- Enthalpy of formation at 0 K
- Gibbs free energy coefficients from 0 to 6000 K (from curve fitting)
- Molecular weight

The number of conserved variables in the solution vector $Q$ is the summation of

- The number of atomic species for equilibrium problems (or the number of molecular species for non-equilibrium problems)
- The number of dimensions of the flow: two or three
- One variable representing the energy equation

The boundary conditions are integer-coded values that correspond to:

- $0 =$ communication with other blocks (interior flow)
- $1 =$ free stream conditions
- $2 =$ supersonic outflow
• 3 = slip condition (inviscid flow, symmetric plane for instance)
• 4 = no slip condition (viscous flow, solid wall)

3.2 Data Curve Fitting

This section describes curve-fits to data contained in the JANAF Thermochemical tables as functions of temperature. The curve-fit coefficients for these data are stored in database files read by the C.F.D. code. A separate file exists for each molecular species.

3.2.1 Curve Fitting of the Equilibrium Constants

The equilibrium constant data were fit to a cubic spline:

\[
\log [K_p(T_r)] = a + bT_r + cT_r^2 + dT_r^3
\]  

(3.1)

where \( T_r \) is the reduced temperature and is found as \((T - T_l)\), where \( T_l \) is the lower temperature of the 100 K temperature interval being considered (For example, if \( T = 1050 \) K, \( T_l = 1000 \) K and \( T_r = 50 \) K).

We show here some curve fittings for the equilibrium constants, as functions of temperature, for \( \text{H}_2\text{O} \) and \( \text{HO} \).
Figure 4: Equilibrium Constant Curve Fit for $\text{H}_2\text{O}$

Figure 5: Equilibrium Constant Curve Fit for $\text{HO}$
3.2.2 Curve Fitting of the Enthalpies and Constant Pressure Specific Heats

The enthalpies $H(T)$ and constant pressure specific heats $C_p(T)$ were also interpolated using a cubic spline curve fitting.

We know that $H(T) - H(T_0) = \int_{T_0}^{T} C_p(T) dT$, \hspace{1cm} (3.2.a)

we find $C_p(T) = \frac{\partial H(T)}{\partial T}$. \hspace{1cm} (3.2.b)

Then, the cubic spline curve fitting was expressed at a particular temperature:

\begin{align*}
H(T) &= a + bT + cT^2 + dT^3 \\
C_p(T) &= b + 2cT + 3dT^2
\end{align*}

(3.3)

We find the curve fitting coefficients $(a,b,c,d)$ for each one hundred Kelvin interval $(T_i, T_{i+1})$ by using a simple matrix inversion as follows:

\[
\begin{bmatrix}
1 & T_i & T_i^2 & T_i^3 \\
0 & 1 & 2T_i & 3T_i^2 \\
1 & T_{i+1} & T_{i+1}^2 & T_{i+1}^3 \\
0 & 1 & 2T_{i+1} & 3T_{i+1}^2
\end{bmatrix}
\begin{bmatrix}
a \\ b \\ c \\ d
\end{bmatrix}
= \begin{bmatrix}
h_i \\ C_{p_i} \\ h_{i+1} \\ C_{p_{i+1}}
\end{bmatrix}
\hspace{1cm} (3.4)
\]

where the 4 x 4 matrix was inverted using a Gaussian elimination procedure.

As can be seen on Figure 6, there is an abrupt change in the curve fit of the specific heat at constant pressure with respect to the temperature around 100 K. This is due to the requirement that $C_p(0) = 0$. This should be of no consequence in this study since the expected temperatures should be on the order of 1000 Kelvin. In future studies, this may need to be re-examined.

35
Figure 6: Cp Curve Fit for $H_2O$

Figure 7: Enthalpy Curve Fit for $H_2O$
3.2.3 Curve Fitting of the Gibbs Free Energy and of its Derivative

These curve fittings use a cubic spline method similar to those seen in the two previous sections. The same way as for the equilibrium constants, we have to enforce the fact that we do not want any inflexion at a data point. This means that for the Gibbs function $G$, or its derivative with respect to the temperature $dG/dT$, at any two consecutive points $(T_1, T_2)$, we have $G''(T_1) = G''(T_2) = 0$, where $G''$ expresses the second derivative with respect to the temperature of the function $G$. The values of the coefficients used for the fitting of the data are stored in files for each species and are read for the particular temperature interval in which the current temperature lies at each iteration, and are then stored in a dynamic array.

![Gibbs Energy Curve Fit for H2O](image)

Figure 8: Gibbs Energy Curve Fit for H$_2$O
3.3 Newton-Raphson Iterative Process

This section illustrates the Newton-Raphson method for the iterative solution of a set of nonlinear equations. This method will be employed in each of the three approaches to solve the composition of the mixture in chemical equilibrium. Consider a set of three nonlinear equations \((f_1, f_2, f_3)\) in three unknowns \((x_1, x_2, x_3)\).

\[
\overline{F} = \begin{pmatrix} f_1(\overline{X}) \\ f_2(\overline{X}) \\ f_3(\overline{X}) \end{pmatrix} = 0
\]

\[
\overline{X} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}
\]

The procedure is initialized with an approximation \(\overline{X}_0\) to \(\overline{X}\). Then, at each iteration, we do the following operations:

- Calculate the Jacobian matrix of the system

\[
J = \frac{\partial \overline{F}}{\partial \overline{X}} = \begin{pmatrix} \frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} & \frac{\partial f_1}{\partial x_3} \\ \frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2} & \frac{\partial f_2}{\partial x_3} \\ \frac{\partial f_3}{\partial x_1} & \frac{\partial f_3}{\partial x_2} & \frac{\partial f_3}{\partial x_3} \end{pmatrix}
\]

(3.6)

- Solve the system for the \(X_i\) increments

\[
J^n \Delta \overline{X}^n = -\overline{F}(\overline{X}^n)
\]

\[
\Delta \overline{X}^n = -\left(J^n\right)^{-1} \overline{F}(\overline{X}^n)
\]

(3.7)

At each iteration, the increment of the unknown variables is calculated by inverting the Jacobian matrix, which is usually done by a Gaussian elimination method. The solution vector at the next step is calculated by: \(\overline{X}_{n+1} = \overline{X}_n - J^{-1} \overline{F}(\overline{X}_n)\), which can be replaced by
\( \overline{X}^{n+1} = \overline{X}^n + \Delta \overline{X}^n \) or \( \overline{X}^{n+1} = \overline{X}^n + \omega \Delta \overline{X}^n \), where \( \omega \) is a relaxation parameter. The process is continued until convergence is achieved. The solution is considered to be converged when the residuals \( \Delta X/X < \varepsilon \) for all the unknown variables \( X \), of the vector \( X \). \( \varepsilon \) is a tolerance defined by the programmer.

### 3.4 Assumptions regarding the Products of Reaction

An assumption was required as to what products will be present from the combustion of fuel (kerosene) and oxidizer (hydrogen peroxide). At first, we assumed the combustion temperature and the mixture pressure to be respectively 1100 Kelvin and 20 bars. These values are typical of predicted test conditions. We first browsed the JANAF tables to look at the values of the equilibrium constants as expressed of log\((K_p)\) for a temperature of 1100 Kelvin and a pressure of 1.0 bar. We only considered species that had a logarithmic value of their equilibrium constant ranging from at least -10.0, except for the carbon.

The species considered after this first sorting were:

- Carbon Dioxide \( \text{CO}_2(g) \), log\((K_p)\) = 18.805
- Carbon Monoxide \( \text{CO} \), log\((K_p)\) = 9.928
- Water \( \text{H}_2\text{O}(g) \), log\((K_p)\) = 8.881
- Hydroxyl \( \text{OH}(g) \), log\((K_p)\) = -1.041
- Methane \( \text{CH}_4(g) \), log\((K_p)\) = -1.447
- Formyl \( \text{HCO}(g) \), log\((K_p)\) = 0.435
- Carbon Suboxide \( \text{C}_3\text{O}_2(g) \), log\((K_p)\) = 7.445
- Formaldehyde \( \text{H}_2\text{CO}(g) \), log\((K_p)\) = 4.005
- Oxygen \( \text{O}(g) \), log\((K_p)\) = -8.603
- Hydrogen \( \text{H}(g) \), log\((K_p)\) = -7.587
Carbon C(g), log(Kp) = -25.869

Diatomci Oxygen O_2(g), log(Kp) = 0.0

Diatomci Hydrogen H_2(g), log(Kp) = 0.0

Carbon graphite (solid) C(gr), log(Kp) = 0.0

After several attempts, we noted that numeric convergence was difficult to achieve with so many species in very little quantity. Preliminary results from these tests suggested, and output from the C.E.A. code confirmed, that we could further limit the number of our products to only six:

- Carbon Dioxide CO_2(g)
- Carbon Monoxide CO
- Water H_2O(g)
- Methane CH_4(g)
- Diatomic Oxygen O_2(g)
- Diatomic Hydrogen H_2(g)

In subsequent calculations, these six were assumed to be the only molecular species present.
3.5 Chemistry Subroutines

3.5.1 Computation using the Equilibrium Constants

This section will explain the implementation of the Newton-Raphson method as applied to the equilibrium constants approach. Experience has shown that performance is improved by holding the total number of moles constant during each iteration. In this way, only the diagonal elements of the Jacobian matrix are non-zero, and the matrix equation reduces to a series of scalar inversions. Also, the 14 x 14 system is solved as an 11 x 11 system for the species in non-standard states, and a linear 3 x 3 system for species in standard states.
\[ f_1 = \frac{P_{CO}}{P_{O_2}} - K_{P_{CO2}} = \frac{n_{CO_2}}{n_{O_2}} - K_{P_{CO2}} = 0 \]

\[ f_2 = \frac{P_{CO}}{(P_{O_2})^{1/2}} - K_{P_{CO}} = \frac{n_{CO}}{(n_{O_2})^{1/2}} \left( \frac{P_{MIX}}{n_{TOTAL}} \right)^{1/2} - K_{P_{CO}} = 0 \]

\[ f_3 = \frac{P_{H_2O}}{(P_{O_2})^{1/2}} - K_{P_{H_2O}} = \frac{n_{H_2O}}{(n_{O_2})^{1/2}} \left( \frac{n_{TOTAL}}{P_{MIX}} \right)^{1/2} - K_{P_{H_2O}} = 0 \]

\[ f_4 = \frac{P_{H_2O}}{(P_{O_2}P_{H_2})^{1/2}} - K_{P_{H_2O}} = \frac{n_{H_2O}}{(n_{H_2}n_{O_2})^{1/2}} - K_{P_{H_2O}} = 0 \]

\[ f_5 = \frac{P_{CH_4}}{(P_{H_2})^{1/2}} - K_{P_{CH_4}} = \frac{n_{CH_4}}{(n_{H_2})^{1/2}} \left( \frac{n_{TOTAL}}{P_{MIX}} \right)^{1/2} - K_{P_{CH_4}} = 0 \]

\[ f_6 = \frac{P_{HCO}}{(P_{O_2}P_{H_2})^{1/2}} - K_{P_{HCO}} = \frac{n_{HCO}}{(n_{H_2}n_{O_2})^{1/2}} - K_{P_{HCO}} = 0 \]

\[ f_7 = \frac{P_{CO_2}}{P_{O_2}} - K_{P_{CO2}} = \frac{n_{CO_2}}{n_{O_2}} - K_{P_{CO2}} = 0 \]

\[ f_8 = \frac{P_{H_2O}}{P_{H_2}} \left( P_{O_2} \right)^{1/2} - K_{P_{H_2O}} = \frac{n_{H_2O}}{n_{H_2}} \left( \frac{n_{TOTAL}}{P_{MIX}} \right)^{1/2} - K_{P_{H_2O}} = 0 \]

\[ f_9 = \frac{P_{H_2O}}{(P_{O_2})^{1/2}} - K_{P_0} = \frac{n_{O}}{(n_{O_2})^{1/2}} \left( \frac{P_{MIX}}{n_{TOTAL}} \right)^{1/2} - K_{P_0} = 0 \]

\[ f_{10} = \frac{P_{H}}{(P_{H_2})^{1/2}} - K_{P_h} = \frac{n_{H}}{(n_{H_2})^{1/2}} \left( \frac{P_{MIX}}{n_{TOTAL}} \right)^{1/2} - K_{P_h} = 0 \]

\[ f_{11} = P_{C(g)} - K_{P_{C(4)}} = n_{C(g)} \left( \frac{P_{MIX}}{n_{TOTAL}} \right) - K_{P_{C(4)}} = 0 \]

\[ f_{12} = 2n_{CO_2} + n_{CO} + n_{H_2O} + n_{H_2} + n_{HCO} + 2n_{CO_2} + n_{H_2} + n_0 + 2n_{O_2} - N_0 = 0 \]

\[ f_{13} = 2n_{H_2O} + n_{H_2} + 4n_{CH_4} + n_{HCO} + 2n_{H_2} + n_0 + 2n_{H} - N_H = 0 \]

\[ f_{14} = n_{CO_2} + n_{CO} + n_{CH_4} + n_{HCO} + 3n_{CO_2} + n_{H_2} + n_{c_2} + n_{C(g)} + 2n_{c_4} - N_c = 0 \]

The first eleven equations are based on the definition of the equilibrium constants. The last three equations represent the atomic species balance for oxygen, hydrogen and carbon. Carbon is present in both solid (graphite, denoted as "gr") and gaseous (denoted as "g") states. The atomic molar concentrations of N_0, N_H and N_C are calculated from the output
atomic densities from the resolution of the Navier-Stokes equations in a particular cell volume as follows:

\[ N_o = \frac{\text{Volume}_{\text{CELL}} \cdot \rho_o}{MW_o} \]
\[ N_H = \frac{\text{Volume}_{\text{CELL}} \cdot \rho_H}{MW_H} \]
\[ N_C = \frac{\text{Volume}_{\text{CELL}} \cdot \rho_C}{MW_C} \]

(3.9)

When the total number of moles in the mixture is constant, the coefficients for the Gaussian matrix are as follows:

\[ a(1,1) = \frac{1}{n_{o_1}} \]
\[ a(2,2) = \frac{1}{n_{o_t}} \sqrt{\frac{P_{\text{MIXTURE}}}{n_{\text{TOTAL}}}} \]
\[ a(3,3) = \frac{1}{\sqrt{n_{o_2} n_{H_2}}} \sqrt{\frac{n_{\text{TOTAL}}}{P_{\text{MIXTURE}}}} \]
\[ a(4,4) = \frac{1}{\sqrt{n_{o_2} n_{H_2}}} \]
\[ a(5,5) = \frac{n_{\text{TOTAL}}}{n_{H_2}^2 P_{\text{MIXTURE}}} \]
\[ a(6,6) = \frac{1}{\sqrt{n_{o_2} n_{H_2}}} \]
\[ a(7,7) = \frac{1}{n_{o_t}} \]
\[ a(8,8) = \frac{1}{\sqrt{n_{o_2} n_{H_2}}} \sqrt{\frac{n_{\text{TOTAL}}}{P_{\text{MIXTURE}}}} \]
\[ a(9,9) = \frac{P_{\text{MIXTURE}}}{n_{\text{TOTAL}}} \]
\[ a(10,10) = \frac{1}{\sqrt{n_{H_2}^2 n_{\text{TOTAL}}}} \sqrt{\frac{n_{\text{TOTAL}}}{P_{\text{MIXTURE}}}} \]
\[ a(11,11) = \frac{P_{\text{MIXTURE}}}{n_{\text{TOTAL}}} \]
\[ a(i,j) = 0, \text{ if } i \neq j, \ i = 1,\ldots,11 \]

(3.10)

Since the matrix is diagonal, we do not actually need to use a Gaussian elimination method and can just solve the solution vector by scalar inversions. The elemental balance equations are then used to calculate the molar concentrations of H₂, O₂ and C(gr) as follows:

\[ n_{o_1} = \frac{\left( N_o - 2n_{CO} - n_{CO} - n_{H_2O} - n_{HO} - n_{HCO} - 2n_{C_0} - n_{CH_3O} - n_o \right)}{2} \]
\[ n_{H_2} = \frac{\left( N_H - 2n_{H_2O} - n_{HO} - 4n_{CH_4} - n_{HCO} - 2n_{CH_2O} - n_H \right)}{2} \]
\[ n_{C(gr)} = \frac{\left( N_C - n_{CO} - n_{CO} - n_{H_2O} - n_{HCO} - 3n_{C_0} - n_{CH_3O} - n_{C(g)} \right)}{2} \]

(3.11)
The subroutine is described by the following flow chart:

![Flow Chart](image)

**Figure 9: Equilibrium Constant Subroutine Flow Chart**

Results and discussion following several tests using this method are detailed in part 4.1.
3.5.2 Computation using Gibbs Free Energy Minimization

The minimization of Gibbs free energy was used to initialize the molar fractions of the six species (CO₂, CO, H₂O, CH₄, H₂ and O₂) considered in our combustion problem. We assume a temperature and a pressure for a particular cell of the grid. We solve the six Lagrangians corresponding to the six different species, three atomic mass balance equations, and a last function representing the total number of moles. The total number of moles is a variable and is included in the ten-component solution vector:

\[ \text{sol} = \begin{bmatrix} n_{\text{CO}_2} & n_{\text{CO}} & n_{\text{H}_2\text{O}} & n_{\text{CH}_4} & n_{\text{H}_2} & n_{\text{O}_2} & \lambda_{\text{H}} & \lambda_{\text{C}} & \lambda_{\text{O}} & n_{\text{TOTAL}} \end{bmatrix}^T \] (3.12)

The flow chart for this subroutine is shown below:

![Gibbs Subroutine Flow Chart](image-url)

Figure 10: Gibbs Subroutine Flow Chart
The Lagrangians are given by:

\[
\begin{align*}
    f_1 &= G^0_{CO_2}(T) + R_u T \left( \ln \left( \frac{n_{CO_2} P_{MIXTURE}}{n_{TOTAL}} \right) + 1 - \sum_{i=1}^{ns} \frac{n_i}{n_{TOTAL}} \right) + \lambda_C + 2 \lambda_O \\
    f_2 &= G^0_{CO}(T) + R_u T \left( \ln \left( \frac{n_{CO} P_{MIXTURE}}{n_{TOTAL}} \right) + 1 - \sum_{i=1}^{ns} \frac{n_i}{n_{TOTAL}} \right) + \lambda_C + \lambda_O \\
    f_3 &= G^0_{H_2O}(T) + R_u T \left( \ln \left( \frac{n_{H_2O} P_{MIXTURE}}{n_{TOTAL}} \right) + 1 - \sum_{i=1}^{ns} \frac{n_i}{n_{TOTAL}} \right) + 2 \lambda_H + \lambda_O \\
    f_4 &= G^0_{CH_4}(T) + R_u T \left( \ln \left( \frac{n_{CH_4} P_{MIXTURE}}{n_{TOTAL}} \right) + 1 - \sum_{i=1}^{ns} \frac{n_i}{n_{TOTAL}} \right) + \lambda_C + 4 \lambda_H \\
    f_5 &= G^0_{H_2}(T) + R_u T \left( \ln \left( \frac{n_{H_2} P_{MIXTURE}}{n_{TOTAL}} \right) + 1 - \sum_{i=1}^{ns} \frac{n_i}{n_{TOTAL}} \right) + 2 \lambda_H \\
    f_6 &= G^0_{O_2}(T) + R_u T \left( \ln \left( \frac{n_{O_2} P_{MIXTURE}}{n_{TOTAL}} \right) + 1 - \sum_{i=1}^{ns} \frac{n_i}{n_{TOTAL}} \right) + 2 \lambda_O \\
    f_7 &= 2n_{H_2O} + 4n_{CH_4} + 2n_{H_2} - N_H \\
    f_8 &= n_{CO_2} + n_{CO} + n_{CH_4} - N_C \\
    f_9 &= 2n_{CO_2} + n_{CO} + n_{H_2O} + 2n_{O_2} - N_O \\
    f_{10} &= \sum_{i=1}^{ns} n_i - n_{TOTAL}
\end{align*}
\]

(3.13)

The total number of moles has already been taken into account inside the solution vector, and is therefore not differentiated with respect to each one of the species, so that the coefficients of the Gaussian matrix are then calculated as follows:
\[ [1]: \quad a(i,i) = \frac{\partial f_i}{\partial n_i} = \frac{R_u T}{n_i} - \frac{R_u T}{n_{TOTAL}}, \quad i = 1, \text{ns} (6) \]

\[ [2]: \quad a(i,k) = \frac{\partial f_i}{\partial n_k} = -\frac{R_u T}{n_{TOTAL}}, \quad i = 1, \text{ns} (6), \ j = 1, \text{ns}; \ j \neq i \]

\[ [3]: \quad a(i,j) = \frac{\partial f_i}{\partial \lambda_j} = a_s, \quad i = 1, \text{ns} (6); \ j = 1, \text{ne} (3: \text{H, C, O}) \]

\[ [4]: \quad a(i,k) = \frac{\partial f_i}{\partial n_{TOTAL}} = -\frac{R_u T}{n_{TOTAL}} \left( 1 - \frac{\sum_{i=1}^{n} n_i}{n_{TOTAL}} \right), \quad i = 1, \text{ns} (6); \ k = 10 \]

\[ [5]: \quad a(ns + j, i) = \frac{\partial f_{ns+j}}{\partial n_i} = a_j, \quad i = 1, \text{ns} (6); \ j = 1, \text{ne} (3) \]

\[ [6]: \quad a(k, i) = \frac{\partial f_k}{\partial n_i} = 1, \quad i = 1, \text{ns} (6); \ k = 10 \]

\[ [7]: \quad a(k, k) = \frac{\partial f_k}{\partial n_k} = -1, \quad k = 10 \] (3.14)

Hence, the 10 x 10 matrix, initialized to zero at the beginning of the subroutine, is filled by the previous coefficients as follows:

\[
\begin{pmatrix}
\vdots & 0 & \cdots & 0 \\
\vdots & \vdots & \cdots & \vdots \\
\vdots & \vdots & \cdots & \vdots \\
\vdots & \vdots & \cdots & \vdots \\
- & - & - & - & - & + & - & + & - \\
- & - & - & - & - & + & - & + & - \\
- & - & - & - & - & + & - & + & - \\
\end{pmatrix}
\]

Results and discussion following several tests using this method are detailed in Part 4.2.
3.5.3 Computation using Helmholtz Free Energy Minimization

The minimization of Helmholtz free energy was the method used to calculate the chemical composition of the grid of our study cases because of the fixed volume of the cells. This part shows the implementation of the Newton-Raphson iterative process to calculate the molar fractions of the six species that were decided to be sufficiently present in the mixture: CO₂, CO, H₂O, CH₄, H₂ and O₂. From Part 2.1.3.3, we get six Lagrangian functions corresponding to the six different species, three functions from atomic mass conservation, and a last function from the definition of the total energy, the last conserved variable. The solution vector is a 10 x 1 matrix as follows:

\[
\text{sol} = \begin{bmatrix} n_{CO_2} & n_{CO} & n_{H_2O} & n_{CH_4} & n_{H_2} & n_{O_2} & \lambda_H & \lambda_C & \lambda_O & T \end{bmatrix}^T \quad (3.15)
\]
The flow chart for this subroutine is shown below:

BEGIN

Computation of Internal Energy

Initial Guesses

Beginning of Newton-Raphson Process

Curve Fitting of data: h, Cp, g at particular Temperature

Computation of Lagrange Functions

Computation of Gaussian matrix coefficients

Call to Gaussian elimination subroutine

Increment of the vector solution

Convergence?

YES

Molar Fractions

Mass Fractions

Calculation of mixture Cp, R and gamma

Outputs: actual P and T

END

Figure 11: Helmholtz Subroutine Flow Chart
The Lagrangian functions are given by

\[ f_1 = G^{0}_{CO}(T) + R_u T \ln \left( \frac{n_{CO} R_u T}{10^5 V} \right) + \lambda_c + 2\lambda_o \]

\[ f_2 = G^{0}_{CO}(T) + R_u T \ln \left( \frac{n_{CO} R_u T}{10^5 V} \right) + \lambda_c + \lambda_o \]

\[ f_3 = G^{0}_{CO}(T) + R_u T \ln \left( \frac{n_{CO} R_u T}{10^5 V} \right) + 2\lambda_H + \lambda_o \]

\[ f_4 = G^{0}_{CH_4}(T) + R_u T \ln \left( \frac{n_{CH_4} R_u T}{10^5 V} \right) + \lambda_c + 4\lambda_H \]

\[ f_5 = G^{0}_{H_2}(T) + R_u T \ln \left( \frac{n_{H_2} R_u T}{10^5 V} \right) + 2\lambda_H \]

\[ f_6 = G^{0}_{O_2}(T) + R_u T \ln \left( \frac{n_{O_2} R_u T}{10^5 V} \right) + 2\lambda_O \]

\[ f_7 = 2n_{H_2O} + 4n_{CH_4} + 2n_{H_2} - N_H \]

\[ f_8 = n_{CO} + n_{CO} + n_{CH_4} - N_C \]

\[ f_9 = 2n_{CO} + n_{CO} + n_{H_2O} + 2n_{O_2} - N_O \]

\[ f_{10} = \sum_{i=1}^{n_l} \left( h_i^0 + h_i(T) \right) n_i \frac{MW(i)}{V} - \sum_{i=1}^{n_l} n_i \frac{R_u T}{V} - \text{Internal Energy} \]  

(3.16)

The coefficients of the Gaussian matrix are calculated as follows:

[1]: \[ a(i,i) = \frac{\partial f_i}{\partial n_i} = \frac{R_u T}{n_i}, \ i = 1,...,ns \]  

[2]: \[ a(i,j) = \frac{\partial f_i}{\partial n_j} = a_{ij}, \ i = 1,...,ns; \ j = 1,...,ne \]  

[3]: \[ a(i,k) = -\frac{\partial f_i}{\partial \lambda_k} = \frac{dG_i^0}{dT} + R_u \ln \left( \frac{n_i R_u T}{10^5 V} \right), \ i = 1,...,ns; \ k = 10 \]  

[4]: \[ a(ns + j,i) = \frac{\partial f_{ns+j}}{\partial n_i} = a_{ij}, \ i = 1,...,ns; \ j = 1,...,ne \]  

[5]: \[ a(k,i) = \frac{\partial f_k}{\partial n_i} = -\frac{R_u T}{V} + \left[ h_i^0 + h_i(T) \right] \frac{MW(i)}{V}, \ i = 1,...,ns; \ k = 10 \]  

[6]: \[ a(k,k) = \sum_{i=1}^{n_l} C_{p,i} (T) \frac{n_i MW(i)}{V} - \sum_{i=1}^{n_l} \frac{n_i R_u T}{V}, \ k = 10 \]
Hence, the ten by ten matrix, initialized to zero at the beginning of the subroutine, is filled by the previous coefficients as follows:

\[
\begin{array}{ccc|ccc|ccc}
\backslash & \\ & \backslash & 0 & \backslash & \backslash & [2] & [3] \\
\backslash & \backslash & [1] & \backslash & \backslash & \backslash & \\
0 & \backslash & \backslash & \backslash & \backslash & \backslash & \\
- & - & - & - & - & + & - & + & - \\
\text{[4]} & | & 0 & | & 0 \\
- & - & - & - & - & + & - & + & - \\
\text{[5]} & | & 0 & | & [6] \\
\end{array}
\]

Results and discussion following several tests using this method are detailed in Part 4.3.
4 Results and Discussions

This part presents the results of the various methods to calculate the species molar concentrations for a cell of our grid in chemical equilibrium. We explain the hypotheses for each method, detail the results and conclude whether the method is relevant to be used in our C.F.D. program. In addition, we include the results of the C.E.A. code tests for the same conditions of pressure, temperature and total number of atomic elements H, C and O for comparison purposes with our methods. The results output from C.E.A. are located in the appendices A, B and C.

4.1 Results of the Method using the Equilibrium Constants

The following pictures display the results of a computation using the equilibrium constants at 1100 Kelvin and 20 bars, for the fourteen species considered. The relaxation factor $\omega$ is equal to 0.01 and the tolerance is set to one percent. We assume the total number of moles in the mixture to be constant, therefore, as explained in Part 3.5.1, the Jacobian matrix is diagonal.
Figure 12: Species Molar Fractions using Equilibrium Constants (1)

Figure 13: Species Molar Fractions using Equilibrium Constants (2)
Figure 14: Species Molar Fractions using Equilibrium Constants (3)

Figure 15: Oscillations of $O_2$, $H_2$ and $C_{(gr)}$
In Figures 12 and 13, the yellow curves represent the molar fractions of C\textsubscript{(g)} (increasing) and CH\textsubscript{4} (decreasing). Convergence to the solution given by the C.E.A. code could not be achieved within one percent after five thousand iterations. Oscillations of species present in very small amount such as C\textsubscript{3}O\textsubscript{2}, C\textsubscript{(gas)}, H\textsubscript{2}CO, O and H destabilize the convergence of the species present in larger quantities. Also, species such as H\textsubscript{2}, O\textsubscript{2} and C\textsubscript{(gr)} show huge oscillations in the first ten iterations (Figure 15). The mixture is, in this case, near stoichiometric conditions. Therefore, by looking at the relative magnitudes of the equilibrium constants, (the larger ones indicate the products that are more likely to form), there should be little quantities of O\textsubscript{2}, H\textsubscript{2}, and CO, because the oxygen should combine with the hydrogen to produce water and with the carbon to produce CO\textsubscript{2}. The rest of the carbon should then combine with the rest of the oxygen to produce CO\textsubscript{2}, and with the remaining hydrogen to form CH\textsubscript{4}. 

Figure 16: Variation of $n_{\text{TOTAL}}$ in the Mixture with the Equilibrium Constants Method
Figure 16 shows that the total number of moles is not constant through the iterative process, but changes by 22% between the initial and final values. As can be seen from the previous graphs, the largest numbers of species present in the mixture at the end of the reaction are monatomic hydrogen and oxygen. Some gaseous carbon is also present. A favorable result, though, is the trace amounts of species such as C$_3$O$_2$, CH$_2$O, OH, HCO and C in the solid state, which is in accordance with the results from C.E.A.

The following table shows the mole fractions from the test after five thousand iterations and displays the C.E.A. results with the same amount of H, O and C atomic elements:

| Species | CO$_2$ | CO | H$_2$O | HO | CH$_4$ | HCO | C$_3$O$_2$ | CH$_2$O | O  | H   | C(g) | O$_2$ | H$_2$ | C(s) |
|---------|-------|----|--------|----|-------|-----|----------|--------|----|-----|------|------|------|------|------|
| Results | 10$^{-13}$ | 10$^{-24}$ | 10$^{-15}$ | 10$^{-15}$ | 10$^{-24}$ | 10$^{-24}$ | 0.06 | 0.87 | 0.07 | 10$^{-24}$ | 10$^{-24}$ | 10$^{-24}$ |
| CEA     | 0.18 | 0.014 | 0.74 | 0 | 10$^{-5}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0.06 | 0 |
| | 100 | 100 | 100 | N/A | 100 | N/A | N/A | N/A | $\infty$ | $\infty$ | $\infty$ | N/A | 100 | N/A |

Table 1: Comparison between Equilibrium Constants and C.E.A. Results

The fuel to oxidizer ratio that we used in this test is close to seven, a value that a preliminary design of the rocket established. C.E.A. outputs only species that are present in a significant amount in the resulting mixture (up to a quantity of 10$^{-5}$ in molar fraction). The results from the C.E.A test are included in appendix A. From those tests, we made the decision to apply the methods of Gibbs and Helmholtz energies minimizations.
4.2 Results of the Method Minimizing Gibbs Free Energy

We ran a test at a pressure of 20 bars and a temperature of 1000 Kelvin. The relaxation factor $\phi$ is equal to 0.01 and the tolerance is set to 1%. The maximum number of iterations within the Newton-Raphson process is set to 1000. Convergence was achieved in 824 iterations. The table below presents the initial guesses, final values and residuals for the species molar fractions, the Lagrange multipliers and the total number of moles in the mixture after convergence.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Initial Guesses</th>
<th>Final Values</th>
<th>Residuals</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O$</td>
<td>0.1</td>
<td>0.4858</td>
<td>1.38 $10^{-5}$</td>
</tr>
<tr>
<td>$H_2$</td>
<td>0.2</td>
<td>$6.938 \times 10^{-2}$</td>
<td>$-9.83 \times 10^{-5}$</td>
</tr>
<tr>
<td>$O_2$</td>
<td>0.3</td>
<td>$1.88 \times 10^{-19}$</td>
<td>$-9.99 \times 10^{-3}$</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>0.2</td>
<td>0.40426</td>
<td>$-1.64 \times 10^{-5}$</td>
</tr>
<tr>
<td>$CO$</td>
<td>0.1</td>
<td>$4.0141 \times 10^{-2}$</td>
<td>$1.63 \times 10^{-4}$</td>
</tr>
<tr>
<td>$CH_4$</td>
<td>0.1</td>
<td>$4.2 \times 10^{-4}$</td>
<td>$1.63 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\lambda_H$</td>
<td>0</td>
<td>$7.14 \times 10^{-8}$</td>
<td>$2.46 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\lambda_O$</td>
<td>0</td>
<td>$2.87 \times 10^{10}$</td>
<td>$2.73 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\lambda_C$</td>
<td>0</td>
<td>$3.84 \times 10^{9}$</td>
<td>$4.48 \times 10^{-5}$</td>
</tr>
<tr>
<td>$n_{TOTAL}$ ($kg.mol$)</td>
<td>$2.40549 \times 10^{-7}$</td>
<td>$2.16313 \times 10^{-7}$</td>
<td>$-1.36 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Table 2: Initial and Final Values and Residuals using Gibbs Method

The initial value for the total number of moles present in the mixture was calculated using Dalton’s law for perfect gas with a volume of one cubic centimeter

$$n_{TOTAL} = \frac{(20 \times 10^5)(0.01)^3}{(8314.3)(1000)}$$

$$n_{TOTAL} = 2.40549 \times 10^{-7} \text{ kg.mol}$$
The following figures display the results for this test.

Figure 17: Molar Fractions using Gibbs Method

Figure 18: Residuals for the Species Concentrations using Gibbs Method
Figure 19: Residuals for the Lagrange Multipliers and $n_{\text{TOTAL}}$ using Gibbs Method

Figure 20: Total Number of Moles using Gibbs Method
As can be seen from the previous graphs, the Gibbs minimization method seems to give some more realistic results. Residuals show a tendency to go to zero (Figures 18 and 19) after two hundred iterations only, except for the one corresponding to $O_2$ present in a very small amount in the mixture. Besides, residuals for the Lagrange multipliers quickly tend to zero, and the residual corresponding to the total number of moles reaches zero almost instantly, meaning that this quantity converges very fast (Figures 19 and 20), with a 11% difference between initial and final values. Including the same amount of atomic concentrations of H, O and C at the same pressure and temperature, we ran a test with the C.E.A. to compare our results. The following table shows the mole fractions from the test after five thousand iterations and displays the C.E.A. results with the same amount of H, O and C atomic elements:

<table>
<thead>
<tr>
<th>Species</th>
<th>$H_2O$</th>
<th>$H_2$</th>
<th>$O_2$</th>
<th>$CO_2$</th>
<th>CO</th>
<th>$CH_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gibbs</td>
<td>0.48580</td>
<td>6.9384 $10^{-2}$</td>
<td>1.9 $10^{20}$</td>
<td>0.40426</td>
<td>4.0141 $10^{-2}$</td>
<td>4.2 $10^{-4}$</td>
</tr>
<tr>
<td>C.E.A.</td>
<td>0.48587</td>
<td>6.9320 $10^{-2}$</td>
<td>0</td>
<td>0.40419</td>
<td>4.021 $10^{-2}$</td>
<td>4.2 $10^{-4}$</td>
</tr>
<tr>
<td>$</td>
<td>\varepsilon(%)</td>
<td>,$</td>
<td>0.02</td>
<td>0.01</td>
<td>N/A</td>
<td>0.01</td>
</tr>
</tbody>
</table>

**Table 3: Comparison between Gibbs Minimization and C.E.A. Results**

The table shows a maximum percentage difference of 0.1 %. C.E.A. considers that $O_2$ is in a too small amount and does not account for it, but so does our subroutine, with a molar concentration of $10^{-20}$. The outputs for this test are included in appendix B. We are now confident that the minimization of the Gibbs function can be successfully used in our program to determine the composition at constant pressure and temperature.
4.3 Results of the Method Minimizing Helmholtz Free Energy

The minimization of Helmholtz free energy is the method that we will use in our CFD code because it represents a chemical equilibrium at constant temperature and volume, the volume being fixed because of our grid. We use the results from the previous test with the minimization of Gibbs energy as inputs for this method. From the Gibbs minimization results, we found for a constant temperature and constant pressure:

- \( n_{\text{TOTAL}} = 2.16313 \times 10^{-7} \text{ kg.mol} \)
- \( V = 0.8992 \text{ cm}^3 \), from Dalton’s law for a perfect gas, at 20 bars and 1000 K
- \( q_0 = -60,118 \text{ kJ/m}^3 \), from the equations of energy, defined as

\[
q_0 = \frac{\sum_{i=1}^{n_i} (h_i^0 + h_i(T)) n_i MW(i)}{V} - \sum_{i=1}^{n_i} \frac{n_i R_i T}{V}, \text{ when there is no kinetic energy involved}
\]

We run a test with the Helmholtz subroutine at a pressure of 20 bars and a cell volume of 0.8992 cm\(^3\) to find the species molar fractions corresponding to a temperature of 1000 Kelvin and an internal energy \( q_0 \) of -60,118 kJ/m\(^3\). The tolerance was set to 1% and, since we wanted to decrease the convergence time, the relaxation factor \( \omega \) followed the formula

\[
\omega = \omega_0 \left( 1 + 99 \frac{\text{iteration}}{\text{iteration}_{\text{MAX}}} \right)
\]

Where

- \( \omega_0 = 0.01 \),
- “iteration” represents the number of the iteration in the Newton-Raphson method,
- “iteration\(_{\text{MAX}}\)” is equal to one thousand.

A poor initial guess for the temperature was deliberately set to 2500 K to verify the convergence of the method to the physical solution, which took 100 iterations.
As a result, with $p_0 = 20$ bars and $n_0$ being the number of moles corresponding to the conditions set above, we find the following ratios:

- $p/p_0 = 1.0035$ (0.35% difference)
- $n/n_0 = 1.000024$ (~ 0% difference)
- $T = 1003.5$ K (0.35% difference).

The table below presents the initial guesses, final values and residuals for the species molar fractions, the Lagrange multipliers and the temperature, as well as the total number of moles in the mixture after convergence.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Initial Guesses</th>
<th>Final Values</th>
<th>Residuals</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_2O</td>
<td>0.45</td>
<td>0.48589</td>
<td>-1.98 $10^{-4}$</td>
</tr>
<tr>
<td>H_2</td>
<td>0.05</td>
<td>0.6921 $10^{-2}$</td>
<td>-2.50 $10^{-3}$</td>
</tr>
<tr>
<td>O_2</td>
<td>0.01</td>
<td>2.0932 $10^{-20}$</td>
<td>-1.25 $10^{-1}$</td>
</tr>
<tr>
<td>CO_2</td>
<td>0.35</td>
<td>0.40399</td>
<td>6.71 $10^{-4}$</td>
</tr>
<tr>
<td>CO</td>
<td>0.13</td>
<td>4.0489 $10^{-2}$</td>
<td>-9.13 $10^{-3}$</td>
</tr>
<tr>
<td>CH_4</td>
<td>0.01</td>
<td>4.1947 $10^{-4}$</td>
<td>-2.04 $10^{-3}$</td>
</tr>
<tr>
<td>$\lambda_H$</td>
<td>0</td>
<td>7.13 $10^{7}$</td>
<td>1.96 $10^{-3}$</td>
</tr>
<tr>
<td>$\lambda_O$</td>
<td>0</td>
<td>2.86 $10^{8}$</td>
<td>2.25 $10^{-3}$</td>
</tr>
<tr>
<td>$\lambda_C$</td>
<td>0</td>
<td>3.83 $10^{7}$</td>
<td>9.40 $10^{-4}$</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>2500</td>
<td>1003.5</td>
<td>-3.76 $10^{-3}$</td>
</tr>
<tr>
<td>$n_{TOTAL}$ (kg.mol)</td>
<td>2.16313 $10^{-7}$</td>
<td>2.16318 $10^{-7}$</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 4: Initial and Final Values and Residuals using Helmholtz Method
The following figures display the results for this test.

Figure 21: Molar Fractions using Helmholtz Method

Figure 22: Temperature Evolution using Helmholtz Method
Figure 23: Residuals for the Molar Fractions using Helmholtz Method

Figure 24: Residuals for Lagrange Multipliers and Temperature using Helmholtz Method
As can be seen from the previous graphs, Helmholtz minimization converges to theoretical results even though the initial guess for the temperature was poor (Figures 21 and 22). Residuals show a tendency to go to zero after only sixty iterations except for the one corresponding to O\textsubscript{2} present in a very small amount in the mixture, which diverges in the first thirty iterations before converging to zero (Figure 23). The residual for the temperature is the fastest to reach a final value, as seen in Figure 23 as well. Besides, it is noticeable from Figure 25 that the total quantity of matter in the mixture, if not constant, varies by a small amount (0.5% at the maximum) while running the Helmholtz method.

We run a test with the C.E.A. to compare our results. We included the same amount of atomic mass concentrations at the same pressure and temperature. The following table shows the mole fractions from the test after five thousand iterations and displays the C.E.A. results with the same amount of H, O, and C atomic masses.
The table shows a maximum percentage of difference of 0.52%. C.E.A. considers that the O₂ amount is too small and does not account for it, but so does our subroutine, with a molar concentration of $10^{-20}$. Results are very comparable to the ones from the Gibbs subroutine. The outputs from this C.E.A. test are included in appendix C at the end of this report.
5 Planned Rocket Combustor Test Case Setup

In a planned continuation of this project, the implementation of the Helmholtz Free Energy minimization routine in a parallel C.F.D. code will be tested on a rocket engine designed by a team of undergraduate senior students at Embry-Riddle. We would like to take the opportunity to thank the Pittsburgh Supercomputer Center for having let us use the computational resources of their cluster. This section describes the engine, its fuel/oxidizer stoichiometry at the design condition, and the computational mesh that will be used.

5.1 Physical Characteristics

The rocket combustion chamber has separate fuel and oxidizer orifices and a convergent-divergent nozzle. Fuel and oxidizer have a good chance to enter the combustion chamber through the injector plate as gases, which simplifies the study. Four sets of injectors are evenly distributed on the injector plate. Each set consists of three oxidizer injectors, and one slightly larger fuel injector. Sketches of the engine assembly and injector plate are provided in the next page.
Net mass flow rates for the fuel and oxidizer are 0.0506 and 0.3544 kg/s respectively.
5.2 Fuel and Oxidizer

The fuel is kerosene, for which we use as an average chemical formula, \( \text{C}_{12}\text{H}_{23} \) [19]. The oxidizer is a ninety percent (by mass) aqueous solution of hydrogen peroxide (\( \text{H}_2\text{O}_2 \)). The oxidizer over fuel mass ratio is seven. The following steps are required in order to determine the various reactants proportions. We know that

\[
\begin{align*}
MW(\text{H}_2\text{O}) &= 18.01528 \text{ kg/kg.mol} \\
MW(\text{H}_2\text{O}_2) &= 34.01468 \text{ kg/kg.mol} \\
MW(\text{C}_{12}\text{H}_{23}) &= 167.3146 \text{ kg/kg.mol}
\end{align*}
\]

and owing to the fact that

\[
\frac{m_{\text{H}_2\text{O}}}{m_\text{FUEL}} = 9
\]

\[
\frac{m_{\text{OX}}}{m_\text{FUEL}} = 7
\]

we can find the number of moles of hydrogen peroxide \( n_{\text{H}_2\text{O}_2} \), with respect to the number of moles of water in the aqueous solution:

\[
n_{\text{H}_2\text{O}_2} = \left( \frac{m_{\text{H}_2\text{O}_2}}{m_{\text{H}_2\text{O}}} \right) \times \left( \frac{MW(\text{H}_2\text{O})}{MW(\text{H}_2\text{O}_2)} \right) n_{\text{H}_2\text{O}}
\]

\[
n_{\text{H}_2\text{O}_2} = (9) \times \left( \frac{18.01528}{34.01458} \right) n_{\text{H}_2\text{O}}
\]

\[
n_{\text{H}_2\text{O}_2} = 4.7667 n_{\text{H}_2\text{O}}
\]

The stoichiometric reaction would then be written as:

\[
\text{C}_{12}\text{H}_{23} + v_{\text{OX}} \left( \frac{4.7667\text{H}_2\text{O}_2 + 1.0\text{H}_2\text{O}}{4.7667 + 1.0} \right) \rightarrow \text{Mixture of Products}
\]
and we can determine $v_{OX}$ knowing the oxidizer over fuel mass ratio:

$$MW(OX) = \frac{4.7667 MW(H_2O_2) + 1.0 MW(H_2O)}{4.7667 + 1.0} = 31.2402 \text{ kg/kg.mol}$$

$$v_{OX} = \left( \frac{m_{OX}}{m_{FUEL}} \right) \left( \frac{MW(C_{12}H_{23})}{MW(OX)} \right) n_{C_{12}H_{23}}$$

$$v_{OX} = \left( \frac{167.3146}{31.2402} \right) n_{C_{12}H_{23}}$$

$$v_{OX} = 37.4902 n_{C_{12}H_{23}} \quad (5.4)$$

For one mole of kerosene, we get the following stoichiometry:

$$C_{12}H_{23} + 37.4902(0.82659H_2O_2 + 0.17341H_2O) \rightarrow \text{Mixture of Products}$$

The atomic fluxes of carbon, hydrogen, and oxygen for the fuel and oxidizer are in the following proportions.

<table>
<thead>
<tr>
<th></th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel (kg.mol)</td>
<td>12.0</td>
<td>23.0</td>
<td>0</td>
</tr>
<tr>
<td>Oxidizer (kg.mol)</td>
<td>0</td>
<td>74.9804</td>
<td>68.4792</td>
</tr>
</tbody>
</table>

Table 6: Atomic Fluxes of Carbon, Hydrogen and Oxygen at the Fuel and Oxidizer
5.3 Structured Mesh Generation

A hexagonal block structured mesh of the engine flow path was constructed. The quarter plane symmetry was used in order to minimize computational resources, at the probable expense of some loss of turbulent structures near the symmetry planes. The engine was designed using CATIA, an industry-standard computer aided design (CAD) software tool. The geometry of the engine was exported in IGS format, and subsequently imported by GAMBIT, and later GRIDGEN, two commercially available computational mesh generation software packages. The final resulting mesh was generated primarily with GRIDGEN.

![Figure 28: Oxidizer Injector Mesh](image)

Figure 28 shows the strategy for structured multiblocking of an axisymmetric injector. Creating a structured topology for the injector face proved challenging. Figure 29 depicts the
topology, which features 95 four-sided surfaces. Note the clustering of grid lines near solid surfaces in both figures, as well as at the origin of shear layers around injector orifices.

![Injector Plate Mesh](image)

**Figure 29: Injector Plate Mesh**

(95 faces)

One hundred and forty-nine points were defined along the longitudinal axis of the nozzle, with clustering near the injector plate to resolve the mixing of the fuel and the oxidizer. The grid cells totaled more than seven million. A crucial consideration of the meshing was to size the blocks forming the mesh in order to achieve an acceptable load balancing. Since the code will be run in parallel, each processor will be assigned a block to work on, separately from the other blocks. Therefore, the slowest processes, namely the ones that work on bigger blocks, determine the overall computational time. It follows that if a mesh has a small number of small blocks, then the corresponding processors will have to wait for the bigger blocks to be done being processed. On the other hand, if our mesh has a greater number of small blocks, then more corresponding processors will have to wait for the rest of the blocks to be processed and the computing time will be higher. Therefore, a very important step
when meshing our nozzle was to make sure that the blocks were approximately the same size.

The one hundred and twenty seven blocks have the following dimensions:

- 8 blocks are $21 \times 21 \times 61$ (24,000 cells)
- 4 blocks are $16 \times 16 \times 149$ (33,000 cells)
- 24 blocks are $21 \times 31 \times 61$ (36,000 cells)
- 26 blocks are $16 \times 21 \times 149$ (44,000 cells)
- 17 blocks are $21 \times 21 \times 149$ (59,200 cells)
- 48 blocks are $21 \times 31 \times 149$ (88,800 cells)

This gives an average of 59,940 cells per block, 79 of them being below that average and 48 blocks being above.
6 Conclusions

In this thesis, we examined an original method to calculate the composition of a non-premixed flow in chemical equilibrium and its implementation in Fortran 90. The code is now ready to run in parallel for various cases. We will later implement the code in parallel on the university cluster and will make actual C.F.D. calculations for various cases. This paper introduced three possible methods to calculate chemical equilibrium by using the equilibrium constants, the minimization of the Gibbs function or the minimization of the Helmholtz function. The equilibrium constants method proved to be less versatile and difficult to converge because of the species in very small amount present in the mixture. However, the minimization of the thermodynamic functions of Gibbs and Helmholtz provided some interesting results. We achieved convergence to results comparable to those from the C.E.A. in less than a thousand iterations for Gibbs and in one hundred iterations for Helmholtz. When solving a very large number of cells, Gibbs method serves quickly to determine initial estimates for initializing the flow field to free stream conditions. Future improvements are still possible in the code of our C.F.D. program. Those include an upwinding of the inviscid fluxes, as opposed to the central difference scheme with artificial dissipation adopted here, in order to increase the spatial resolution. Implementing a flux difference-splitting scheme, for example, would also increase the accuracy in the boundary layer region. We could also test various diffusion models to see which one fits best the species diffusion within a combustion chamber. Our implementation of the Helmholtz subroutine takes eighty iterations to converge within one percent, whereas the C.E.A. code converges in only twenty iterations. This procedure is called for each cell of the grid, so it would be very profitable to gain some efficiency in the computing time by decreasing the amount of iterations by calculating a suitable relaxation factor at each iteration.
7 Reference


[18] Fluent user’s guide for equilibrium and non-equilibrium formulations and schemes as provided through the university at www.fluentusers.com.


APPENDIX A - C.E.A. Code Results: First Test
To compare with the results from the Equilibrium Constants Method
't problem' dataset

problem test tp p(bar)=20,t(k)=500,1000,1100,1500

react
fuel= C moles = 12 0
fuel= H moles = 22 0
oxid= H moles = 74 44
oxid= O moles = 67 48233
output short
end

THERMODYNAMIC EQUILIBRIUM PROPERTIES AT ASSIGNED
TEMPERATURE AND PRESSURE

<table>
<thead>
<tr>
<th>REACTANT</th>
<th>MOLES</th>
<th>ENERGY</th>
<th>TEMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>FUEL C</td>
<td>12 0000000</td>
<td>0 000</td>
<td>0 000</td>
</tr>
<tr>
<td>FUEL H</td>
<td>22 0000000</td>
<td>0 000</td>
<td>0 000</td>
</tr>
<tr>
<td>OXIDANT H</td>
<td>74 4400000</td>
<td>0 000</td>
<td>0 000</td>
</tr>
<tr>
<td>OXIDANT O</td>
<td>67 4823300</td>
<td>0 000</td>
<td>0 000</td>
</tr>
</tbody>
</table>

O/F= 6.94339 %FUEL = 12.589077 R,EQ RATIO= 1.070206 PHI,EQ RATIO= 1.156553

THERMODYNAMIC PROPERTIES

| P, BAR   | 20 000 | 20 000 | 20 000 | 20 000 |
| T, K     | 500 00 | 1000 00 | 1100 00 | 1500 00 |
| RHO, KG/CU M | 1 0979 | 1 5 2774 | 0 4 7970 | 0 3 5178 |
| H, KJ/KG | -11364 | 2 -10282 | 9 -10078 | 0 -9217 04 |
| U, KJ/KG | -11546 | 4 -10661 | 9 -10494 | 9 -9785 58 |
| G, KJ/KG | -15565 | 2 -20160 | 6 -21158 | 3 -25326 0 |
| S, KJ/(KG)(K) | 8 4019 | 9 8777 | 10 0730 | 10 7393 |
| M, (1/n) | 22 821 | 21 940 | 21 937 | 21 936 |
| (dLV/dLP)t | -1 00030 | -1 00028 | -1 00003 | -1 00000 |
| (dLV/dLT)p | 1 0063 | 1 0036 | 1 0003 | 1 0000 |
| Cp, KJ/(KG)(K) | 1 6786 | 2 0353 | 2 0691 | 2 2290 |
| GAMMA_s | 1 2812 | 1 2304 | 1 2244 | 1 2049 |
| SON VEL,M/SEC | 483 1 | 682 9 | 714 5 | 827 7 |

MOLE FRACTIONS

<table>
<thead>
<tr>
<th></th>
<th>0 02016</th>
<th>0 00007</th>
<th>0 00001</th>
<th>0 00000</th>
</tr>
</thead>
<tbody>
<tr>
<td>*CO</td>
<td>0 00000</td>
<td>0 01185</td>
<td>0 01584</td>
<td>0 02908</td>
</tr>
<tr>
<td>*CO2</td>
<td>0 18714</td>
<td>0 18738</td>
<td>0 18343</td>
<td>0 17019</td>
</tr>
<tr>
<td>*H2</td>
<td>0 00120</td>
<td>0 06655</td>
<td>0 06281</td>
<td>0 04959</td>
</tr>
<tr>
<td>H2O</td>
<td>0 79149</td>
<td>0 73415</td>
<td>0 73792</td>
<td>0 75114</td>
</tr>
</tbody>
</table>

* THERMODYNAMIC PROPERTIES FITTED TO 20000 K
APPENDIX B - C.E.A. Code Results: Second Test
To compare with the results from the Minimization of Gibbs free energy problem test tp p(bar)=20,t(k)=500,1000,1500,2000

react
fuel=C moles = 0 444821
oxid=H moles = 1 112048
oxid=O moles = 1 334461
output short
end

THERMODYNAMIC EQUILIBRIUM PROPERTIES AT ASSIGNED TEMPERATURE AND PRESSURE

<table>
<thead>
<tr>
<th>REACTANT</th>
<th>MOLES</th>
<th>ENERGY</th>
<th>TEMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>FUEL</td>
<td>C</td>
<td>0 4448210</td>
<td>0 000</td>
</tr>
<tr>
<td>OXIDANT</td>
<td>H</td>
<td>1 1120480</td>
<td>0 000</td>
</tr>
<tr>
<td>OXIDANT</td>
<td>O</td>
<td>1 3344610</td>
<td>0 000</td>
</tr>
</tbody>
</table>

O/F= 4 20608 %FUEL= 19 208309 R,EQ RATIO= 1 083333 PHI,EQ RATIO= 1 142857

THERMODYNAMIC PROPERTIES

P, BAR  20 000  20 000  20 000  20 000  20 000
T, K     500 00  1000 00  1500 00  2000 00
RHO, KG/CU M  1 4150  1 6904  0 4 4566  0 3 3421 0
H, KJ/KG  -10066 7 -9080 61 -8179 17 -7236 23
U, KJ/KG   -10208 0 -9379 55 -8627 95 -7834 65
G, KJ/KG    -13480 5 -17230 3 -21499 4 -26080 2
S, KJ/(KG)(K)  6 8276 8 1497 8 8801 9 4220
M,(l/n)  29 412 27 814 27 791 27 788
(dLV/dLP)t  -1 00022 -1 00158 -1 00000 -1 00005
(dLV/dLT)p  1 0046 1 0229 1 0000 1 0016
Cp, KJ/(KG)(K)  1 3773 1 8534 1 8381 1 9400
GAMMAas  1 2609 1 2007 1 1944 1 1830
SON VEL,M/SEC 422 2 599 1 732 1 841 4

MOLE FRACTIONS

<table>
<thead>
<tr>
<th></th>
<th>MOLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>0 02918</td>
</tr>
<tr>
<td>*CO</td>
<td>0 00001</td>
</tr>
<tr>
<td>*CO2</td>
<td>0 44120</td>
</tr>
<tr>
<td>*H</td>
<td>0 00000</td>
</tr>
<tr>
<td>*H2</td>
<td>0 00007</td>
</tr>
<tr>
<td>H2O</td>
<td>0 52875</td>
</tr>
<tr>
<td>*OH</td>
<td>0 00000</td>
</tr>
</tbody>
</table>

* THERMODYNAMIC PROPERTIES FITTED TO 20000 K
APPENDIX C - C.E.A. Code Results: Third Test
First test with \( \text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O} + \text{H} + \text{OH} \)

-problem test tp \( p(\text{bar})=20, t(\text{k})=500,1000,1500,2000 \)

"reactants" dataset

WARNING: DID NOT RECOGNIZE test (INPUT)

\( \text{fuel} = \text{C} \) moles = 0.44489847
\( \text{oxid} = \text{H} \) moles = 1.11187788
\( \text{oxid} = \text{O} \) moles = 1.33435900

output short

THERMODYNAMIC EQUILIBRIUM PROPERTIES AT ASSIGNED TEMPERATURE AND PRESSURE

<table>
<thead>
<tr>
<th>REACTANT</th>
<th>MOLES</th>
<th>ENERGY KJ/KG-MOL</th>
<th>TEMP K</th>
</tr>
</thead>
<tbody>
<tr>
<td>FUEL C</td>
<td>0.4448985</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>OXIDANT H</td>
<td>1.1118779</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>OXIDANT O</td>
<td>1.3343590</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

\( \text{O}/\text{F} = 4, \text{FUEL} = 19, \text{R}, \text{EQ} \text{ RATIO} = 1.083468, \text{PHI}, \text{EQ} \text{ RATIO} = 1.143081 \)

THERMODYNAMIC PROPERTIES

| P, BAR | 20.000 | 20.000 | 20.000 | 20.000 |
| T, K   | 500.00 | 1000.00| 1500.00| 2000.00|
| \( \rho, \text{KG/CU M} \) | 1.4151 | 1.6903 | 0.4565 | 0.3320 |
| H, KJ/KG | -100662 | -907971 | 71.8178 | 21.7235 |
| U, KJ/KG | -102075 | -937865 | 86.2700 | 783372 |
| G, KJ/KG | -13479H | -17229T | -21498S | -26079V |
| S, KJ/(KG)(K) | 6.8273 | 8.1497 | 8.8803 | 9.4221 |

| (dLV/dLP)t | -1.00022 | -1.00159 | -1.00000 | -1.00005 |
| (dLV/dLT)p | 1.0046   | 1.0230   | 1.0000   | 1.0016 |
| \( \text{Cp}, \text{KJ}/(\text{KG})(\text{K}) \) | 1.3773 | 1.8542 | 1.8381 | 1.9400 |
| \( \text{GAMMAs} \) | 1.2609 | 1.2007 | 1.1944 | 1.1830 |
| \( \text{SON VEL, M/SEC} \) | 422.1 | 599.1 | 732.1 | 841.4 |

MOLE FRACTIONS

| CH4  | 0.02923 | 0.00042 | 0.00000 | 0.00000 |
| CO   | 0.00001 | 0.04028 | 0.07243 | 0.08431 |
| CO2  | 0.44128 | 0.40420 | 0.37210 | 0.36017 |
| H    | 0.00000 | 0.00000 | 0.00000 | 0.00006 |
| H2   | 0.00087 | 0.06941 | 0.03885 | 0.02700 |
| H2O  | 0.52862 | 0.48569 | 0.51662 | 0.52832 |
| OH   | 0.00000 | 0.00000 | 0.00000 | 0.00013 |

* THERMODYNAMIC PROPERTIES FITTED TO 20000 K