

## EVALUATION OF THERMOCHEMICAL PROPERTIES AND COMBUSTION TEMPERATURE FOR LOX/LH<sub>2</sub> REACTION SCHEMES

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**Abstract.** *Nine chemical reaction models for the pair hydrogen/oxygen are studied, taking into account different conditions found in real rocket engines. For chemical equilibrium, it is used equilibrium constants methodology. Comparisons between two models with eight chemical species have shown that the model with 18 chemical reactions has converged with smaller time than the model with 6 chemical reactions. It was also seen that the most complex model (eight species and 18 chemical reactions) has been the fastest, or nearly the one, among models with six and eight species. Results from models with six species have been very close to the ones obtained with eight species. A model with only four species, however, can have significant errors. Both combustion temperature and thermochemical properties depend only on the chemical species taken into account by the used model. Comparisons among results from the implemented program (Gibbs 1.3), CEA and Teqworks (these last two, programs from NASA) have shown that Gibbs 1.3 evaluates correctly both combustion temperature and mixtures of gases thermochemical properties.*

**Keywords:** *Chemical Reaction Models, Chemical Equilibrium, Combustion Temperature.*

### 1. INTRODUCTION

Liquid-propellant rocket systems are the main space propulsion systems. They allowed the conquest of space during the last 30 years (Habiballah et al., 1998). There are many liquid-propellant combinations, like oxygen/jet fuel (used in Atlas, Thor and Saturn booster) and oxygen/hydrogen (used in Centaur and Saturn upper stages, Space Shuttle and in Vulcain engine); LOX/LH<sub>2</sub> (liquid oxygen/liquid hydrogen) systems, however, are and probably will continue to be the preferred propulsion systems for space propulsion for the next decades (Haidn and Habiballah, 2003).

Most of rocket engines have cooling systems, which allow a longer lifetime for the entire device. One of the most used cooling systems for large rocket engines is the regenerative one. The prediction of heat transfer characteristics in a regeneratively cooled rocket combustion engine is one of the most important and most challenging tasks in the design work of a high performance engine (Fröhlich et al., 1993).

The knowledge of compounds formed at LOX/LH<sub>2</sub> combustion is the first step for a complete study involving combustion mixture gases flow, heat transfer and coolant pressure drop in a real rocket engine. At high temperatures, such as those found in rocket thrust chambers, effects of dissociation become important and new species must be considered

(Anderson Jr., 1993). Dissociation reactions are known to be endothermic, so temperatures achieved by combustion reactions are lower than ones predicted without dissociation effects.

Thermodynamic properties of species are required to define properly an equilibrium composition of a mixture of gases. Such properties can be easily taken from thermodynamic tables and/or graphics. In this work, however, it is used the method shown by McBride et al. (1993), in which libraries for thermodynamic and transport properties of pure species can be found. The essential properties used in this work are constant-pressure specific heat, enthalpy and Gibbs free energy, whose utility lies on the fact that the implemented computational code uses equilibrium constants methodology.

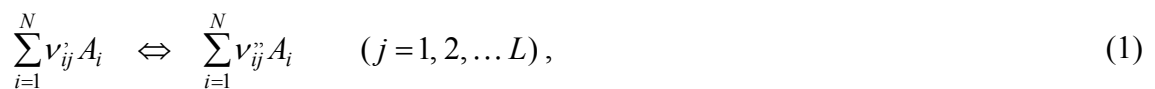
Nine different reaction models are used to obtain equilibrium composition. At the simplest, it is considered only three chemical species: H<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O, without chemical dissociation reactions. In the most complete scheme, eight species (H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, H, O, OH, H<sub>2</sub>O<sub>2</sub> and HO<sub>2</sub>) and 18 chemical reactions are studied.

These models have been implemented using Fortran PowerStation 4.0. The implemented program, called Gibbs 1.3, was run at PC Pentium III, 750 MHz, with 786 MB RAM. The codes and the executable version of Gibbs 1.3, as well as a complete report containing all tests made, can be found at [ftp://ftp.demec.ufpr.br/CFD/projetos/cfd5/relatorio\\_tecnico\\_1/](ftp://ftp.demec.ufpr.br/CFD/projetos/cfd5/relatorio_tecnico_1/).

Two different kinds of comparisons are presented in this work. Firstly, five couples of temperature and pressure values are chosen, intending to cover all range of values found in a real rocket thrust chamber; results are compared with those obtained from CEA (Glenn Research Center, 2005) and Teqworks (Gordon and McBride, 1971), both programs from NASA. Secondly, it is studied the combustion temperature of H<sub>2</sub> and O<sub>2</sub> reactions at different oxidant/fuel mass ratios and combustion pressures; results are compared with programs CEA and Teqworks and, for some cases, with other results from literature.

## 2. CHEMICAL REACTIONS

The methodology used in this work to obtain chemical equilibrium parameters of a mixture of gases can be found in Kuo (1986) and is briefly shown in this section. Firstly, it is considered a chemical reaction in the form:



where:  $A$  represents each chemical specie symbol,  $i$  corresponds to the number of each chemical specie,  $N$  is the total number of chemical species,  $j$  corresponds to a specific chemical reaction,  $L$  is the total number of chemical reactions,  $\nu_{ij}^{\prime}$  and  $\nu_{ij}^{\prime\prime}$  are, in this order, the stoichiometric coefficients of chemical specie  $i$  in reaction  $j$  existent in reagents and products.

For each single chemical reaction  $j$ , there is a specific equilibrium constant ( $K_j$ ), based on partial pressures ( $p_i$ ). This constant shows how the direct and the reverse ways of reaction  $j$  are related at a specific temperature and can be calculated by

$$K_j = \prod_{i=1}^N p_i^{(\nu_{ij}^{\prime\prime} - \nu_{ij}^{\prime})}. \quad (2)$$

However, there is another form to obtain the same constant; in this case, it is needed the Gibbs free energy change for that reaction, which can be evaluated by

$$\Delta G_j = \sum_{i=1}^N \nu_{ij}'' g_i - \sum_{i=1}^N \nu_{ij}' g_i, \quad (3)$$

where  $g_i$  corresponds to the Gibbs free energy of specie  $i$ . Such value is calculated with the methodology presented by McBride et al. (1993), in which values of constant-pressure specific heat ( $c$ ), enthalpy ( $h$ ) and Gibbs free energy ( $g$ ), in this order, can be estimated by

$$c_i = Ru \left( a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \right)_i, \quad (4)$$

$$h_i = Ru T_i \left( a_1 + a_2 \frac{T}{2} + a_3 \frac{T^2}{3} + a_4 \frac{T^3}{4} + a_5 \frac{T^4}{5} + \frac{a_6}{T} \right)_i, \quad (5)$$

$$g_i = Ru T_i \left( a_1 (1 - \ln T) - a_2 \frac{T}{2} - a_3 \frac{T^2}{6} - a_4 \frac{T^3}{12} - a_5 \frac{T^4}{20} + \frac{a_6}{T} - a_7 \right)_i, \quad (6)$$

where: coefficients  $a_k$  have particular values for every single chemical specie  $i$ ,  $Ru$  is the universal constant for perfect gases (8.314510 J/mol-K) and  $T$  corresponds to the absolute temperature (in Kelvin) at which the property is been evaluated. Based on these pieces of information,  $K_j$  can also be obtained by

$$K_j = \exp\left(-\frac{\Delta G_j}{RuT}\right). \quad (7)$$

Another chemical or thermodynamic relations are of use in this work, such as mean constant-pressure specific heat ( $c$ ) and density ( $\rho$ ) of mixture. Because of this, they are related in the following. The first useful quantity is the mean molecular weight, which can be evaluated by

$$M = \frac{1}{n} \sum_{i=1}^N n_i M_i = \sum_{i=1}^N X_i M_i. \quad (8)$$

In Eq. (8),  $n$  is the total number of moles,  $M_i$  is the molecular weight of chemical specie  $i$  and  $X_i$  is the molar fraction of chemical specie  $i$ , depends on total pressure ( $p$ ) and can be obtained by

$$X_i = \frac{n_i}{n} = \frac{p_i}{p}. \quad (9)$$

Assuming an ideal gas behaviour, it can be used the perfect gas equation to calculate the overall gas mixture density ( $\rho$ ) by

$$\rho = \frac{p}{RT}. \quad (10)$$

Two other properties of importance presented are mass fraction ( $Y_i$ ) for each specie  $i$  and constant-pressure specific heat ( $c$ ), given, in this order, by

$$Y_i = \frac{\rho_i}{\rho} = X_i \frac{M_i}{M} = \frac{n_i M_i}{nM} \quad (11)$$

and

$$c = \sum_{i=1}^N Y_i c_i . \quad (12)$$

The last three properties evaluated by program Gibbs are the gases mixture constant ( $R$ ), the ratio of specific heats ( $\gamma$ ) and the total concentration of mixture ( $C$ ), given, respectively, by

$$R = 1000 \frac{Ru}{M}, \quad (13)$$

$$\gamma = \frac{c}{(c - R)}, \quad (14)$$

and

$$C = \sum_{i=1}^N C_i = \frac{p}{RuT}. \quad (15)$$

Every property calculated by Eqs. (8) to (15) are given as exit results, when program Gibbs 1.3 is run.

## 2.1 Numerical models for chemical equilibrium

Nine different chemical reaction models are studied in this work and implemented at Gibbs 1.3. These models have 3, 4, 6 or 8 chemical species and from zero to 18 dissociation chemical reactions. A summarize of all the used models is presented below.

From Table 1, it can be shown that there are some models with same species and same number of chemical reactions, like models 3 and 4. However, they differ from one dissociation equation at least, reason for considering them independent models.

### Model 0

Model 0 is the simplest of all models implemented at Gibbs 1.3. Dissociation effects are not taken into account by this model and, because of this, it has the worst results at high temperatures. The importance of this model, however, is its equations, which are used by the other models. Its global reaction equation is given by



where  $a$  is a function of informed value for oxidant/fuel mass ratio, obtained by

$$a = OF \frac{M_3}{M_2}. \quad (17)$$

In Eq. (17),  $M_2$  and  $M_3$  are, in this order, the molecular weight of molecular hydrogen ( $H_2$ ) and the molecular weight of molecular oxygen ( $O_2$ ). Coefficients  $b$ ,  $d$  and  $f$ , from Eq. (16), are evaluated by mass conservation of atomic species (atomic hydrogen and atomic oxygen), resulting in three cases:

Table 1. Chemical equilibrium reaction models implemented in Gibbs 1.3

Model	$L$	$N$	Species	Observations
0	0	3	$H_2O, O_2, H_2$	–
1	1	3	$H_2O, O_2, H_2$	–
2	2	4	$H_2O, O_2, H_2, OH$	–
3	4	6	$H_2O, O_2, H_2, OH, O, H$	4 reactions with 3 <sup>rd</sup> body – Barros et al. (1990) and Smith et al. (1987)
4	4	6	$H_2O, O_2, H_2, OH, O, H$	Svehla (1964)
5	8	6	$H_2O, O_2, H_2, OH, O, H$	Barros et al. (1990)
7	8	6	$H_2O, O_2, H_2, OH, O, H$	Smith et al. (1987)
10	6	8	$H_2O, O_2, H_2, OH, O, H, HO_2, H_2O_2$	4 reactions from model 3 and 2 from Kee et al. (1990)
9	18	8	$H_2O, O_2, H_2, OH, O, H, HO_2, H_2O_2$	Kee et al. (1990)

Case 1: stoichiometric composition, where

$$a = \frac{1}{2}, \quad b = 1, \quad d = f = 0. \quad (18)$$

Case 2: oxidant-rich mixture ( $O_2$ ), where

$$a > \frac{1}{2}, \quad b = 1, \quad d = a - \frac{1}{2}, \quad f = 0. \quad (19)$$

Case 3: fuel-rich mixture ( $H_2$ ), where

$$a < \frac{1}{2}, \quad b = 2a, \quad d = 0, \quad f = 1 - 2a. \quad (20)$$

At this model, the number of moles for the chemical specie  $i$  ( $n_i$ ) is evaluated by

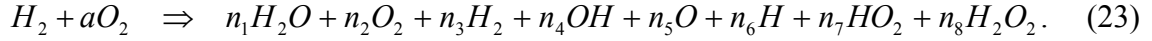
$$n_1 = b, \quad n_2 = d, \quad n_3 = f, \quad n = n_0 \quad (21)$$

and, by definition, the total number of moles for products, without chemical dissociation, is obtained by

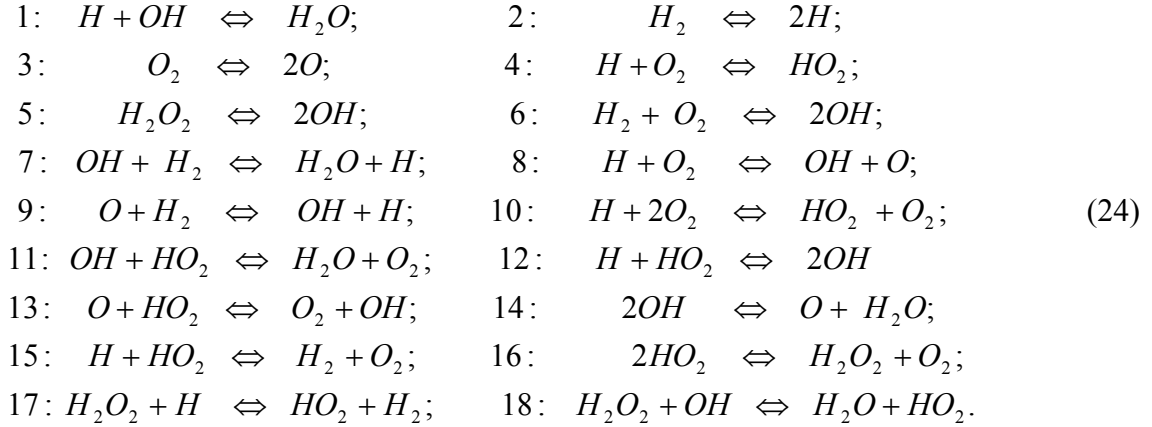
$$n_0 = b + d + f. \quad (22)$$

## Model 9

Model 9 is the most complex one implemented at Gibbs 1.3: eight species and eighteen different reaction equations are assumed. This is the same model used by Kee et al. (1990), at Chemkin program. Global reaction equation is given by



And dissociation equations related to this model are:



The number of moles for each specie  $i$  ( $n_i$ ) can be evaluated by mass conservation. In this case, it must be count on the global reaction equation and the reaction degree for every single dissociation equation ( $\varepsilon_j$ ), resulting in

$$\begin{array}{l}
 n_1 = b + \varepsilon_1 + \varepsilon_7 + \varepsilon_{11} + \varepsilon_{14} + \varepsilon_{18}, \\
 n_2 = d - \varepsilon_3 - \varepsilon_4 - \varepsilon_6 - \varepsilon_8 - \varepsilon_{10} + \varepsilon_{11} + \varepsilon_{13} + \varepsilon_{15} + \varepsilon_{16}, \\
 n_3 = f - \varepsilon_2 - \varepsilon_6 - \varepsilon_7 - \varepsilon_9 + \varepsilon_{15} + \varepsilon_{17}, \\
 n_4 = -\varepsilon_1 + 2\varepsilon_5 + 2\varepsilon_6 - \varepsilon_7 + \varepsilon_8 + \varepsilon_9 - \varepsilon_{11} + 2\varepsilon_{12} + \varepsilon_{13} - 2\varepsilon_{14} - \varepsilon_{18}, \\
 n_5 = 2\varepsilon_3 + \varepsilon_8 - \varepsilon_9 - \varepsilon_{13} + \varepsilon_{14}, \\
 n_6 = -\varepsilon_1 + 2\varepsilon_2 - \varepsilon_4 + \varepsilon_7 - \varepsilon_8 + \varepsilon_9 - \varepsilon_{10} - \varepsilon_{12} - \varepsilon_{15} - \varepsilon_{17}, \\
 n_7 = \varepsilon_4 + \varepsilon_{10} - \varepsilon_{11} - \varepsilon_{12} - \varepsilon_{13} - \varepsilon_{15} - 2\varepsilon_{16} + \varepsilon_{17} + \varepsilon_{18}, \\
 n_8 = -\varepsilon_5 + \varepsilon_{16} - \varepsilon_{17} - \varepsilon_{18}, \\
 n = n_0 - \varepsilon_1 + \varepsilon_2 + \varepsilon_3 - \varepsilon_4 + \varepsilon_5 - \varepsilon_{10}.
 \end{array} \quad (25)$$

The resulting system of equations, which must be solved in order to obtain the composition at chemical equilibrium, is presented in following.

$$\begin{aligned}
 K_1 p n_4 n_6 &= n_1 n, & K_2 n_3 n &= n_6^2 p, & K_3 n_2 n &= n_5^2 p, \\
 K_4 p n_2 n_6 &= n_7 n, & K_5 n_8 n &= n_4^2 p, & K_6 n_2 n_3 &= n_4^2, \\
 K_7 n_3 n_4 &= n_1 n_6, & K_8 n_2 n_6 &= n_4 n_5, & K_9 n_3 n_5 &= n_4 n_6, \\
 K_{10} p n_2 n_6 &= n_7 n, & K_{11} n_4 n_7 &= n_1 n_2, & K_{12} n_6 n_7 &= n_4^2, \\
 K_{13} n_5 n_7 &= n_2 n_4, & K_{14} n_4^2 &= n_1 n_5, & K_{15} n_6 n_7 &= n_2 n_3, \\
 K_{16} n_7^2 &= n_2 n_8, & K_{17} n_6 n_8 &= n_3 n_7, & K_{18} n_4 n_8 &= n_1 n_7.
 \end{aligned} \tag{26}$$

## 2.2 Algorithm for chemical equilibrium

Gibbs 1.3 chemical equilibrium algorithm is presented in this section. It consists of ten steps, listed below:

- 1) Definition of data: reactive model number, temperature ( $T$ ), total pressure ( $p$ ), oxidant/fuel mass ratio ( $OF$ ) and numeric parameters (number of iterations and tolerances).
- 2) Reading of thermodynamic coefficients ( $a_{ki}$ ) of Eqs. (4) to (6).
- 3) Evaluation of coefficients of Eq. (16):  $a$  based on Eq. (17) and  $b$ ,  $d$  and  $f$  by Eq. (18), (19) or (20), depending on case.
- 4) Initialization of reaction degrees ( $\varepsilon_j$ ) for all dissociation reaction, with null-value.
- 5) Evaluation of initial number of moles for every single reactive model specie ( $n_i$ ) and total number of moles ( $n$ ), based on variables from items 3 and 4.
- 6) Evaluation of Gibbs free energy for each single specie ( $g_i$ ) by Eq. (6), Gibbs free energy change by Eq. (3) and equilibrium constant based on partial pressure for reaction  $j$  by Eq. (7).
- 7) Iterative evaluation, for the first dissociation reaction ( $\varepsilon_i$ ), by Newton-Raphson method (Turns, 1996), with calculations made until the maximum number of iterations (itimax) or the tolerance (tol\_e) is achieved. This is made for the second dissociation reaction and so on, until the last reaction ( $L$ ).
- 8) Number of moles actualization for every single specie ( $n_i$ ) and total number of moles ( $n$ ), with obtained results for  $\varepsilon_j$  calculated in item 7.
- 9) Evaluation of total number of moles variation ( $\Delta n$ ). Return to item 7 until the maximum number of iterations (itemax) is achieved or while  $\Delta n$  is greater than the chosen tolerance (tol\_n).
- 10) Evaluation of mixture properties defined by Eqs. (8) to (15).

## 3. COMBUSTION

Combustion temperature determination (also know as adiabatic flame temperature) is, basically, the same problem of chemical equilibrium with a small modification: only the temperatures (or enthalpies) of reagents are known. The problem is, simply, to equalize the enthalpy of reagents with the enthalpy of products. However, as the composition of gas mixture is dependent on the temperature, an iterative method for obtaining the combustion temperature is needed. In this work, it was used a methodology based on bisection method (Chapra and Canale, 1994), with chemical equilibrium parameters calculated by equations

found in Kuo (1986), and presented in last sections. The same chemical reaction models presented in Table 1 are valid for combustion temperature determination code implemented.

### 3.1 Algorithm for adiabatic combustion

The implemented algorithm for adiabatic combustion temperature determination is presented in this section. It consists of 15 steps, listed below:

- 1) Definition of data: reactive model number, temperature or enthalpy of reagents, total pressure ( $p$ ), oxidant/fuel mass ratio (OF) and numeric parameters (iteration numbers and tolerances).
- 2) Reading of thermodynamic coefficients ( $a_{ki}$ ) of Eqs. (4) to (6).
- 3) Evaluation of coefficients of Eq. (16):  $a$  based on Eq. (17) and  $b$ ,  $d$  and  $f$  by Eq. (18), (19) or (20), depending on case.
- 4) Initialization of reaction degrees ( $\varepsilon_j$ ) for all dissociation reaction, with null-value.
- 5) Evaluation of initial number of moles for every single reactive model specie ( $n_i$ ) and total number of moles ( $n$ ), based on variables from items 3 and 4.
- 6) Evaluation of total enthalpy of reagents by

$$H_R = h_{fuel} + a h_{oxidant} . \quad (27)$$

- 7) First guess: the combustion temperature is considered to be 3150 K (mean value between 300 and 6,000K).
- 8) Evaluation of Gibbs free energy for each single specie ( $g_i$ ) by Eq. (6), Gibbs free energy change by Eq. (3) and equilibrium constant based on partial pressure for reaction  $j$  by Eq. (7).
- 9) Iterative evaluation, for the first dissociation reaction ( $\varepsilon_j$ ), by Newton-Raphson method (Turns, 1996), with calculations made until the maximum number of iterations (itimax) or the tolerance (tol\_e) is achieved. This is made for the second dissociation reaction and so on, until the last reaction ( $L$ ).
- 10) Number of moles actualization for every single specie ( $n_i$ ) and total number of moles ( $n$ ), with obtained results for  $\varepsilon_j$  calculated in item 9.
- 11) Evaluation of total number of moles variation ( $\Delta n$ ). Return to item 9 until the maximum number of iterations (itemax) or while  $\Delta n$  is greater than the chosen tolerance (tol\_n).
- 12) Evaluation of total enthalpy of products by Eq. (28):

$$H_P = \sum_{i=1}^N n_i h_i . \quad (28)$$

- 13) New estimative for the combustion temperature with bisection method (Chapra e Canale, 1994).
- 14) Evaluation of temperature variation ( $\Delta T$ ) between old and new temperature. Return to item 8 until the maximum number of iterations (itcmax) is achieved or while  $\Delta T$  is greater than the chosen tolerance (tol\_Tc).
- 15) Evaluation of mixture properties defined by Eqs. (8) to (15).



## 4. NUMERICAL RESULTS

Chemical reaction models have been implemented using Fortran PowerStation 4.0 and the resulting program (Gibbs 1.3) was run in a PC Pentium III, 750 MHz, with 786 MB RAM. Two different kinds of problems were studied: firstly, chemical equilibrium calculation, in which both combustion chamber temperature and pressure are known; secondly, combustion temperature evaluation, in which only the enthalpies of reagents and the chamber pressure were known and temperature of reactions, as well as chemical equilibrium composition, is one of the expected results.

### 4.1 Chemical equilibrium

Five different problems were studied, intending to cover all the range of values found in a rocket thrust chamber: temperatures vary between 600 and 4,000 K, and pressures, between 0.002 and 20 MPa. Oxidant/fuel mass ratio chosen was the stoichiometric one (7.936682739), because this is the mass ratio, which offers the greatest difficulties for numerical convergence. The chosen tolerance to solve  $\varepsilon(j)$  (tol\_e) was  $10^{-12}$ , the same value for the chosen tolerance to solve the total number of moles  $n$  (tol\_n); and the maximum number of iterations to evaluate the total number of moles  $n$  (itemax) was fixed on 50,000, which is the same value for maximum number of iterations to evaluate the dissociation rate for each reaction  $\varepsilon(j)$  (itimax). For each problem, the nine chemical reaction models were used and the results were compared with those obtained from CEA and Teqworks, both programs from NASA, which include the nine species: the eight ones considered in Models 9 and 10 from program Gibbs 1.3 and ozone (O<sub>3</sub>).

Table 2. Thermochemical properties obtained for chemical equilibrium from programs Gibbs 1.3, CEA and Teqworks for a temperature of 4,000 K and pressure of 20 MPa

Model	$M$ (kg/kmol)	$\rho$ (kg/m <sup>3</sup> )	frozen $c$ (J/kg.K)	frozen $\gamma$ (adim.)	$R$ (J/kg.K)	$C$ (mol/cm <sup>3</sup> )	cpu time (s)
0	18.015	10.8336	3,295.5	1.1629	461.53	6.0136e-4	0.00
1	16.865	10.1421	3,300.0	1.1756	493.00	6.0136e-4	0.00
<b>2</b>	<b>16.196</b>	<b>9.7395</b>	<b>3,288.8</b>	<b>1.1850</b>	<b>513.37</b>	<b>6.0136e-4</b>	<b>0.00</b>
3	15.536	9.3425	3,293.5	1.1940	535.19	6.0136e-4	0.02
4	15.536	9.3425	3,293.5	1.1940	535.19	6.0136e-4	0.02
<b>5</b>	<b>15.536</b>	<b>9.3425</b>	<b>3,293.5</b>	<b>1.1940</b>	<b>535.19</b>	<b>6.0136e-4</b>	<b>0.01</b>
7	15.536	9.3425	3,293.5	1.1940	535.19	6.0136e-4	0.01
10	15.537	9.3433	3,293.6	1.1940	535.14	6.0136e-4	0.04
<b>9</b>	<b>15.537</b>	<b>9.3433</b>	<b>3,293.6</b>	<b>1.1940</b>	<b>535.14</b>	<b>6.0136e-4</b>	<b>0.01</b>
CEA	15.516	9.3309	3,290.8	---	---	---	---
Teqworks	15.503	9.3230	---	---	---	---	---

As the results from the other defined problems have similar behaviour, only the results from problem 1, in which are found the highest temperature (4,000 K) and pressure (20 MPa), are shown in this work. In this case, high temperature effects must be considered for a correct estimative of species molar fractions, as well as other thermochemical properties of gases mixture. Tables 2 to 5 summarize some of the most important results found.

Table 3. Comparative errors for thermochemical properties among some Gibbs 1.3 models and Teqworks (CEA results taken as reference)

Comparative error (%)	$M$ (kg/kmol)	$\rho$ (kg/m <sup>3</sup> )	frozen $c$ (J/kg.K)
Model 2	-4.38	-4.38	0.061
Model 5	-0.13	-0.12	-0.082
Model 9	-0.14	-0.13	-0.085
Teqworks	-0.084	0.085	---

Table 4. Mass fractions results for a temperature of 4,000 K and a pressure of 20 MPa

Model	H <sub>2</sub> O	O <sub>2</sub>	H <sub>2</sub>	OH	O	H	HO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	O <sub>3</sub>
0	1.0000e-0	0	0	---	---	---	---	---	---
1	8.6362e-1	1.2112e-1	1.5260e-2	---	---	---	---	---	---
<b>2</b>	<b>7.7532e-1</b>	<b>7.7639e-2</b>	<b>1.7462e-2</b>	<b>1.2958e-1</b>	---	---	---	---	---
3	7.5268e-1	7.7291e-2	1.7347e-2	1.2886e-1	2.1134e-2	2.6914e-3	---	---	---
4	7.5268e-1	7.7291e-2	1.7347e-2	1.2886e-1	2.1134e-2	2.6914e-3	---	---	---
<b>5</b>	<b>7.5268e-1</b>	<b>7.7291e-2</b>	<b>1.7347e-2</b>	<b>1.2886e-1</b>	<b>2.1134e-2</b>	<b>2.6914e-3</b>	---	---	---
7	7.5268e-1	7.7291e-2	1.7347e-2	1.2886e-1	2.1134e-2	2.6914e-3	---	---	---
10	7.5214e-1	7.6915e-2	1.7376e-2	1.2865e-1	2.1082e-2	2.6935e-3	9.2804e-4	2.1200e-4	---
<b>9</b>	<b>7.5214e-1</b>	<b>7.6915e-2</b>	<b>1.7376e-2</b>	<b>1.2865e-1</b>	<b>2.1082e-2</b>	<b>2.6935e-3</b>	<b>9.2804e-4</b>	<b>2.1200e-4</b>	---
CEA	7.4839e-1	7.4654e-2	1.7424e-2	1.3508e-1	2.0636e-2	2.6850e-3	9.2359e-4	2.0703e-4	2.6050e-6
Teqworks	7.478e-1	7.8259e-2	1.7690e-2	1.318e-1	2.1167e-2	2.7045e-3	5.6768e-4	5.534e-13	1.3402e-6

Table 5. Comparative errors for mass fractions among some Gibbs 1.3 models and Teqworks (CEA results taken as reference)

Comparative error	H <sub>2</sub> O	O <sub>2</sub>	H <sub>2</sub>	OH	O	H	HO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	O <sub>3</sub>
Model 2	-2.7e-2	-3.0e-3	-3.8e-5	5.5e-3	2.1e-2	2.7e-3	9.2e-4	2.1e-4	2.6e-6
Model 5	-4.3e-3	-2.6e-3	7.7e-5	6.2e-3	-5.0e-4	-6.4e-6	9.2e-4	2.1e-4	2.6e-6
Model 9	-3.8e-3	-2.3e-3	4.8e-5	6.4e-3	-4.5e-4	-8.5e-6	-4.4e-6	-5.0e-6	2.6e-6
Teqworks	5.9e-4	-3.6e-3	-2.7e-4	3.3e-3	-5.3e-4	-2.0e-5	3.6e-4	2.1e-4	1.3e-6

The cpu time shown in Table 2 is evaluated with a internal command of Fortran PowerStation 4.0, called “timef”, and is evaluated only for the calculation routine implemented. The comparative error shown in Table 5 can be evaluated by

$$Error = Y_{CEA} - Y_{Gibbs \text{ or } Teqworks} \quad (29)$$

where  $Y$  can be a thermochemical property or a mass fraction. For results shown in Table 3, this  $Error$  must be divided by  $Y_{CEA}$  and multiplied by 100.

It can be seen, from Table 2, that models considering chemical dissociation, with the same number of species (such as models 3, 4, 5 and 7) have same results for thermochemical parameters. A briefly view on results presented in Table 4 helps to explain this fact: these models have exactly the same mass fraction configuration. It does not matter the chemical scheme assumed, but only the species taken into account by the model.

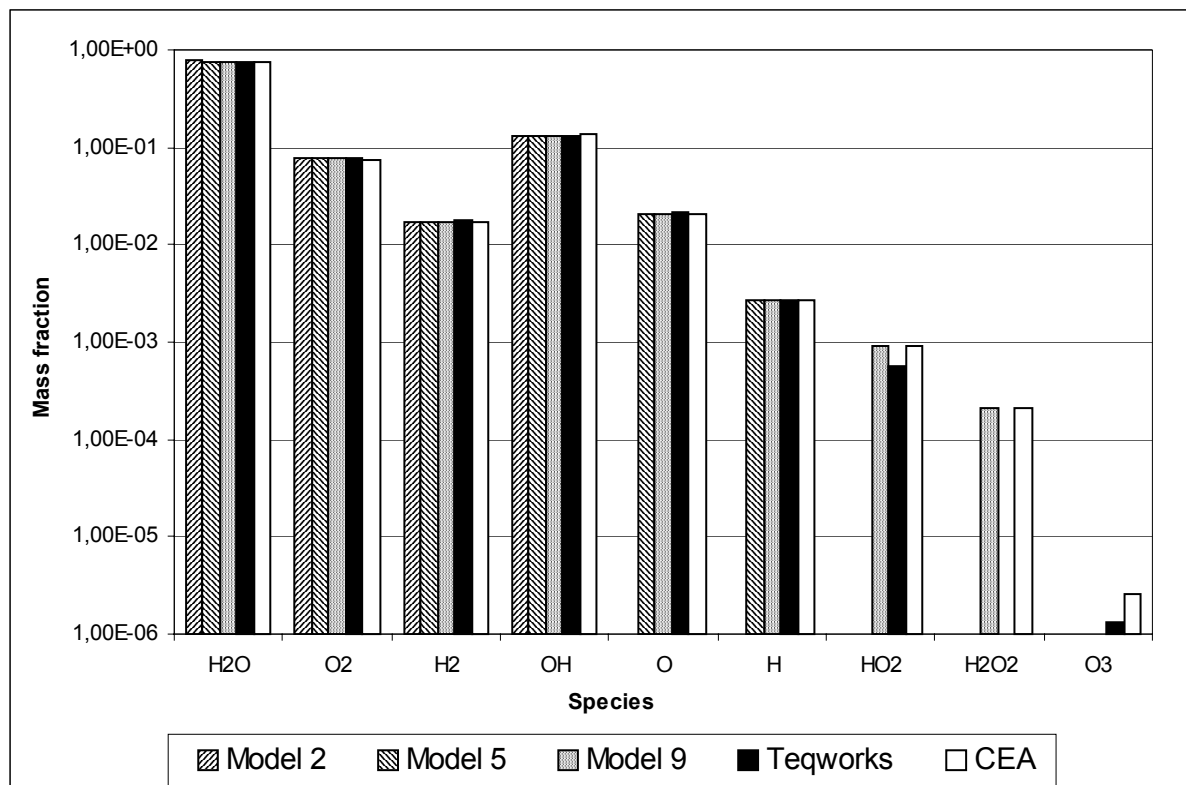


Figure 1 – Chemical composition for equilibrium at 4,000 K and 20 MPa.

Results from model 9 of Gibbs 1.3 have the same accuracy found in results obtained by Teqworks, when both programs are compared with results of CEA. Maximum errors found for global parameters are 0.15% for Gibbs 1.3 (model 9) and 0.085% for Teqworks; about mass fractions, the errors are  $6.4 \times 10^{-3}$  and  $3.6 \times 10^{-3}$ , for Gibbs 1.3 and Teqworks, respectively. Results from other models, however, have also good accuracy. Figure 1 shows the chemical mass fractions for a mixture of gases at 4,000 K and 20 MPa of pressure. As can be seen, model 5, which has six species, has results very close to the ones from model 9 and this conclusion agreed with the other studied problems, not shown in this work. Otherwise, a model with only four species (such as model 2) does not predict properly the chemical composition and the thermochemical properties for the gases mixture at high temperatures; under these conditions, this model can have significant errors.

## 4.2 Combustion temperature

For combustion temperature evaluation, seventeen different problems were studied. Only the temperature of oxidant (LOX) and fuel (LH<sub>2</sub>) were kept constant, with values of 90.17 K (corresponding to a enthalpy of  $-12,979$  J/mol) and 20.27 K (corresponding to  $-9,012$  J/mol), respectively. Comparisons were made with results obtained from programs CEA and Teqworks and, when it was possible, with other literature sources. The chosen tolerance to solve  $\varepsilon(j)$  (tol\_e) was  $10^{-12}$ , the same value for the chosen tolerance to solve the total number of moles  $n$  (tol\_n); and the maximum number of iterations to evaluate the total number of moles  $n$  (itemax) was fixed on 5,000, which is the same value for maximum number of iterations to evaluate the dissociation rate for each reaction  $\varepsilon(j)$  (itimax). The maximum number of iterations for solving the combustion temperature  $T_c$  (itcmax) was chosen to be 500. All the studies were made in a PC Pentium III, 750 MHz, with 786 MB RAM.

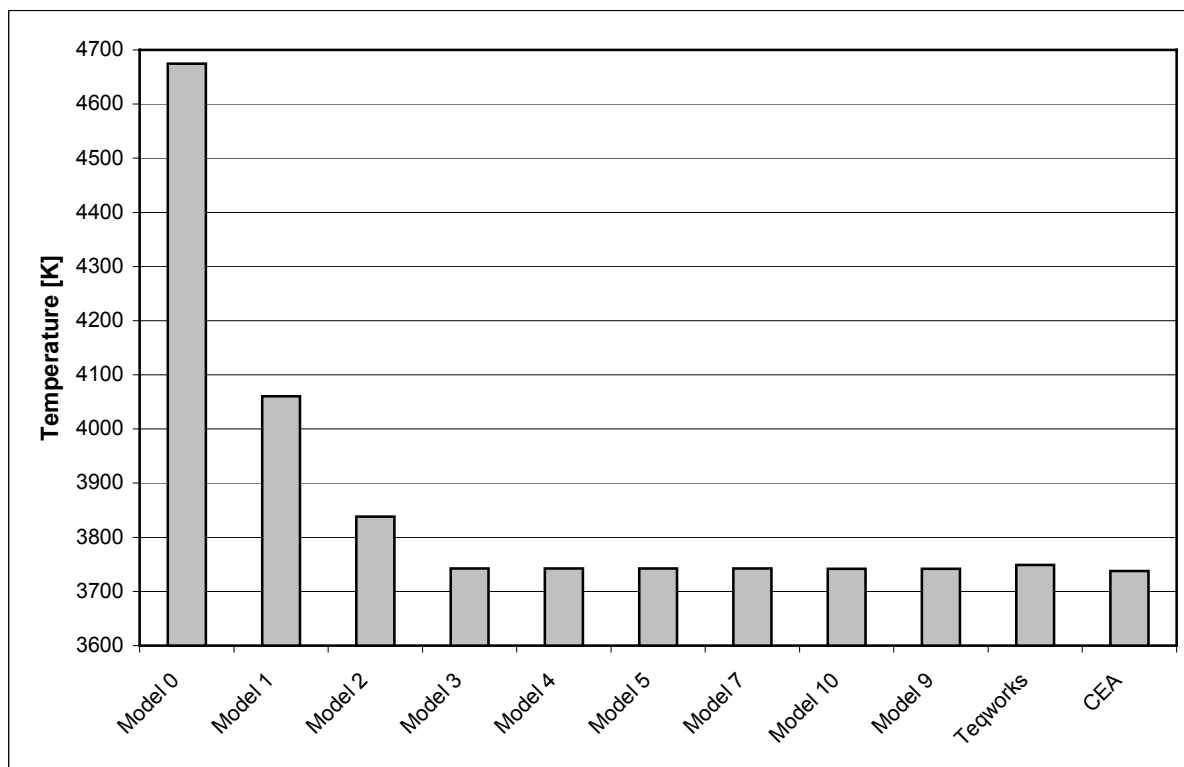


Figure 2 – Combustion temperature evaluated for a chamber pressure of 20 MPa.

Table 6. Combustion temperatures evaluated with programs Gibbs, Teqworks and CEA, for a chamber pressure of 20 MPa

Model	Tc Gibbs [K]	Tc CEA [K]	Error Gibbs* [%]	Tc Teqworks [K]	Error Teqworks* [%]	Gibbs cpu time [s]
0	4674.85		-25			0
1	4060.30		-8.6			0.01
2	3838.08		-2.7			0.05
3	3742.51		-0.13			0.56
4	3742.51	3737.73	-0.13	3748.86	-0.30	0.50
5	3742.51		-0.13			0.23
7	3742.51		-0.13			0.35
10	3741.97		-0.11			0.92
9	3741.97		-0.11			0.39

\* CEA results are taken as reference.

As can be seen from Fig. 2 and Table 6, model 0, which involves three species and no dissociation reaction, overestimates the combustion temperature in 25% for a pressure of 20 MPa. For another problem, in which the pressure value is 2 MPa, the evaluated error is 37%. Model 1, which counts on three species and only one dissociation reaction, has better results, with errors of about 8.6% and 11% for pressures of 20 MPa and 2 MPa, respectively. Model 2, with four species and two dissociation reactions, counts on errors, for pressures of 20 MPa and 2 MPa (in this order), of 2.7% and 4.1%. The best models, however, are the ones with six and eight species. The maximum error for the models with six species was 0.13%, while the maximum error for the models with eight species was 0.11%. Both of them have better results than the ones obtained with program Teqworks, whose errors were 0.30% and 0.19% for

pressures of 20 MPa and 2 MPa, respectively. In all comparisons made, CEA results were taken as reference. It must also be noted that model 9, which has the major complexity, is not the slowest: its convergence was faster than two models with six species and one with eight species. Cpu time was evaluated with an internal command of Fortran PowerStation 4.0, called “timef”.

Table 7. Comparison of combustion temperatures obtained with programs Gibbs (model 9) and CEA, and other sources from literature.

Total pressure [MPa]	Oxidant/fuel mass ratio (OF)	Tc CEA [K]	Tc Gibbs (model 9) [K]	Error Gibbs* [%]	Tc another source [K]	Error* [%]
20	2	1797.78	1796.65	0.063	[Tw] 1798.71	-0.052
20	4	2974.69	2976.10	-0.047	[Tw] 2986.92	-0.41
20	6	3595.43	3599.98	-0.13	[Tw] 3610.55	-0.42
20	10	3644.31	3649.47	-0.14	[Tw] 3658.22	-0.38
20	12	3507.10	3513.33	-0.17	[Tw] 3523.28	-0.46
20	14	3368.28	3374.95	-0.20	[Tw] 3385.28	-0.50
20	16	3234.72	3241.35	-0.20	[Tw] 3251.62	-0.52
20.241	6.00	3596.61	3601.17	-0.13	[Wang, 1993] 3639.0	-1.2
0.51676	8	3237.61	3240.86	-0.10	[Kim, 1991] 3300	-1.9
0.51676	16	2964.90	2970.91	-0.20	[Kim, 1991] 3073	-3.6
6.8948	4.13	2998.45	3000.31	-0.062	[Huzel, 1992] 3013	-0.49
6.8948	4.83	3235.70	3238.85	-0.097	[Huzel, 1992] 3251	-0.47
6.8948	3.40	2668.70	2669.55	-0.032	[Sutton, 1992] 2959	-11
6.8948	4.02	2954.33	2956.01	-0.057	[Sutton, 1992] 2999	-1.5
6.8948	4.00	2946.10	2947.75	-0.056	[Sarner, 1966] 2977	-1.0

\* CEA results are taken as reference. Tw = Teqworks

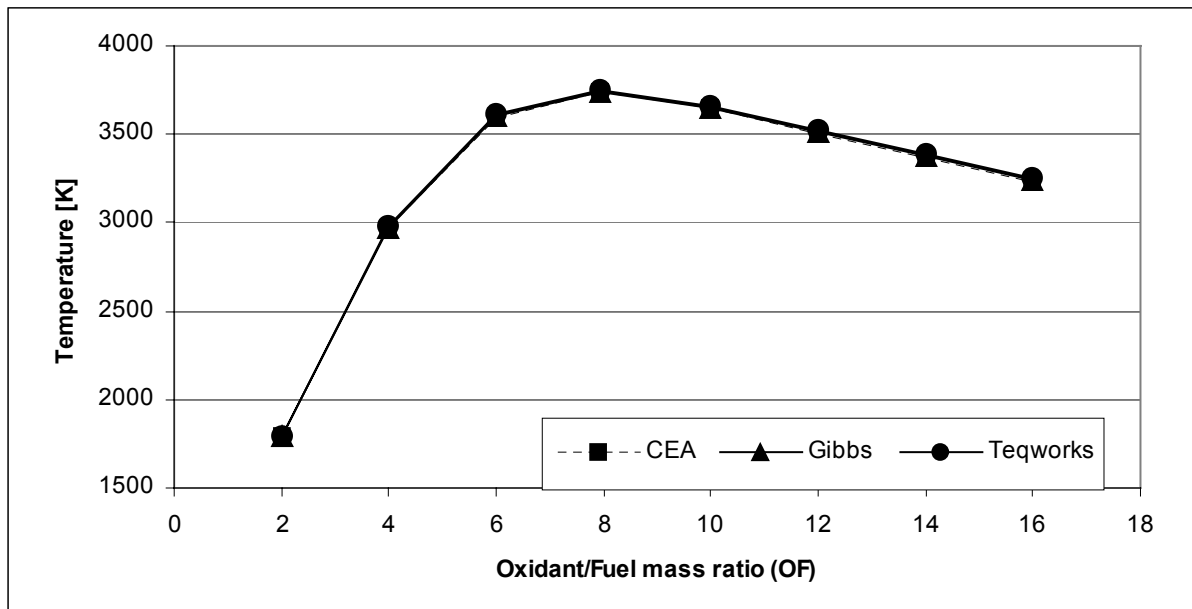


Figure 3 – Combustion temperature as function of OF ratio; total pressure: 20 MPa.

Figure 3 shows the behaviour of combustion temperature as function of OF ratio, for a total pressure of 20 MPa. The maximum temperature achieved corresponds to a OF ratio of about 7.9367, which is the stoichiometric condition. It can be seen that results from Gibbs (model 9), CEA and Teqworks are nearly coincident. In fact, when results obtained by

programs Gibbs and Teqworks are compared with those ones from CEA, minor errors are found for Gibbs results (except for a *OF* ratio of 2, for which Teqworks results are better).

Table 7 provides a series of data, in which program Gibbs results are compared with CEA and other ones, including some from literature. It can be noted that Gibbs results are very close to those ones provided by program CEA. While Gibbs errors are between 0.032 and 0.20%, the other results from literature present errors in the range between 0.47 and 11%. Based on this, it can be affirmed that Gibbs provides good estimates for combustion temperature problems.

## 5. CONCLUSION

A program for prediction of thermochemical properties at chemical equilibrium for a mixture of gases was implemented using equilibrium constants methodology and Fortran PowerStation 4.0 language. This code, called Gibbs, evaluates also combustion temperature for a mixture of hydrogen/oxygen. Chemical reaction schemes implemented varied from a model with only three species, without chemical dissociation reactions (called model 0) and a model with eight species and 18 chemical dissociation reactions (model 9). Validation of results was made comparing those obtained from program Gibbs with ones from other sources, such as CEA and Teqworks, both programs from NASA.

It was found that global variables, like total density or total specific heat, depend only on the species taken into account by the used model, in as much as mass fractions obtained are equivalent. However, computational time needed for convergence is not equal for models with same species: against the common sense, models with more chemical reactions were, in general, faster than the ones with less reactions.

Comparisons made with results from Gibbs, CEA and Teqworks have shown a good accuracy of program Gibbs for evaluation of thermochemical properties and combustion temperature for a mixture of gases. Taking CEA results as reference, it was found that program Gibbs agrees with Teqworks about magnitude of errors. And the differences in results between Gibbs and CEA are smaller than the ones found between CEA and some results from literature, for determination of combustion temperature.

Models with six species have shown good results, when compared with eight species models. In some cases, however, model 9, which is the most complex one, has the best results and is the fastest one. Whether the use of a six species model is desired, it is recommended model 5, which is the fastest among six species models, or model 9, whether a eight species model is required.

As written at introduction, the codes and an executable version of Gibbs 1.3, as well as a complete report (in Portuguese) containing all tests made, can be found at [ftp://ftp.demec.ufpr.br/CFD/projetos/cfd5/relatorio\\_tecnico\\_1/](ftp://ftp.demec.ufpr.br/CFD/projetos/cfd5/relatorio_tecnico_1/).

### *Acknowledgements*

The authors would acknowledge Federal University of Paraná (UFPR), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and The “UNIESPAÇO Program” of The Brazilian Space Agency (AEB) by physical and financial support given for this work. The second author would, also, acknowledge his professors and friends, by discussions and other forms of support.

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