FAST NUMERICAL CODE FOR PREDICTING PROPELLANTS PERFORMANCE

Radu D. Rugescu[1], Sorin Aldea[2]

[1] University Politehnica of Bucharest, Bucharest, ROMANIA, rugescu@yahoo.com
[2] University Politehnica of Bucharest, Bucharest, ROMANIA, sormarald@yahoo.com

Abstract: The propulsive performance of several O-C-H propellants for space propulsion application is investigated through computational prediction and experimental proof, with focus on the effects of chemical equilibrium in water-gas reaction. The correct prediction of the propulsive efficiency of chemical propellants for space propulsion application is the key component of space launchers design and manufacturing. Previous observations of some deviations of this global reaction between the combustion products from chemical equilibrium at elevated temperatures suggest that this chemical equilibrium could have a visible impact on the propulsive efficiency of the propellants. A general computational method was developed and used to reveal possible deviations from the chemical equilibrium and the effect this could have over the specific impulse of rocket engines, powered by chemical propellants. The contribution is the proprietary numerical code that offers a reliable means of such prediction with a minimum amount of computer processing. Results are presented for a series of chemical propellants of immediate interest for the NERVA orbital launcher, developed under the CNMP contract 82076.
Keywords: thermochemistry, combustion, chemical equilibrium, rocket engines, space launchers

1. INTRODUCTION

Analytical prediction of the specific impulse of chemical propellants through thermochemical computations is part of a long history of chemical engineering. Minute thermochemical computations were performed in Germany [1] before WW-2, during the development of modern rocket technology for military applications [2]. Early works of 1930 paved the way for modern investigations [3], although the basics of quantitative mathematical treatment of combustion goes far early to the works of Van't Hoff [4].

A well-known general method for thermochemical computations, suited for electronic computers [5], supplied the basis for all future developments of chemical equilibrium computations. During the 1950's new European and Russian developments led to publication of large volumes thermochemical predictions of rocket propellants for space flight [6], [7]. In Rumania, the works of the thermochemistry of combustion started during 1950's and 1960's. Recent developments are largely performed either in US [8] or in countries that entered recently into the space age [19], [17].

Equilibrium computation of the result of chemical combustion with mostly gaseous products is based on well-established tables of thermodynamic properties of species. They are ordinarily performed within a temperature range from zero to 6000 K. The most known values are summarized [11], [12] and they are continuously updated and added with new chemicals, as for example along the "*Active Thermochemical Tables*" program [13]. Despite the high development level and the high confidence in thermochemical predictions, the chemical equilibrium assumption is not always confirmed. A general computational method is presented for predicting the performance of propellants.

2. DISSOCIATION OF GASSES INTO A NON-ATOMIC BASIS

In order to allow determining the effect of chemical equilibrium of water-gas reaction, a general computational method is applied [14], when the basis of formation of the combustion products consists of the three non-atomic substances

$$CO_2, \quad CO, \quad H_2. \tag{1}$$

Besides this basis, the following 14 gaseous combustion products are considered as significantly present in the combustion chamber at elevated temperature and pressure,

$$H_2O, HO, O_2, HCO, CH_2O, H_2O_2, HO_2, CH_3, CCO, CH_2, CH_4, C_2H_4, H, O \tag{2}$$
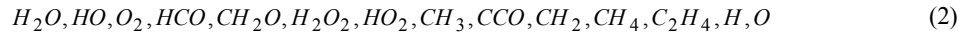
giving a total of 17 species to be considered as a result of regular combustion. According to their chemical formulae, the formation of these products from O–C–H atoms (called *atomic basis*) may be written according as

$$\sum_{j=1}^{l} a_{ij} A_j = C_i \ , \ i{=}1, s \tag{3}$$

where in this case $l{=}3$ and $s{=}17$, or in matrix form [15] for the s species present in the mixture,

$$[a](A)=(C). \tag{4}$$

The brackets denote column vectors and the square brackets denote matrices. To take an example, for $s{=}14$ species from the above mentioned list (2) the matrix of formation from the atomic basis $(A)^T \equiv (O, C, H)$ is

$$
\begin{bmatrix}
2 & 1 & 0 \\
1 & 1 & 0 \\
0 & 0 & 2 \\
1 & 0 & 2 \\
1 & 0 & 1 \\
1 & 1 & 1 \\
1 & 1 & 2 \\
2 & 0 & 2 \\
2 & 0 & 1 \\
0 & 1 & 3 \\
1 & 2 & 0 \\
0 & 1 & 2 \\
0 & 1 & 4 \\
0 & 2 & 4 \\
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\quad
\begin{array}{ll}
2O + C = CO_2 & \textit{Carbon Dioxide} \\
O + C = CO & \textit{Carbon Monoxide} \\
2H = H_2 & \textit{Hydrogen, diatomic} \\
O + 2H = H_2O & \textit{Water, gas} \\
O + H = HO & \textit{Hydroxil} \\
O + C + H = HCO & \textit{Formyl} \\
O + C + 2H = CH_2O & \textit{Formaldehyde} \\
2O + 2H = H_2O_2 & \textit{Hydrogen Peroxide} \\
2O + H = HO_2 & \textit{Hidroperoxil} \\
C + 3H = CH_3 & \textit{Methyl} \\
O + 2C = CCO & \textit{Carbonyl Carbene} \\
C + 2H = CH_2 & \textit{Methylene} \\
C + 4H = CH_4 & \textit{Methane} \\
2C + 4H = C_2H_4 & \textit{Ethane} \\
\quad O, \ \textit{basis} & \\
\quad C, \ \textit{basis} & \\
\quad H, \ \textit{basis} &
\end{array}
\tag{5}
$$

The water gas reaction, involving a global and reciprocal equilibrium between the gaseous dominant combustion products carbon dioxide, carbon monoxide, hydrogen and water, is well known for playing a central role in the chemistry of O–C–H combustion [16]. We may write it according to adopted conventions in the form

$$CO_2 + H_2 \rightarrow H_2O + CO \tag{6}$$

therefor we adopt the basis (1) as the new basis of formation for the species in (2). The dissociation of the 14 molecular compounds listed in (2) into the new basis (1) may be directly expressed by intuitively finding the stoichiometric coefficients, or by mathematically deriving of the new matrix of formation $[b]$ from the old matrix $[a]$ as described in the following.

The formation, or dissociation, of the species from the new basis (B_j) cu j=1,2,3 is governed by the new matrix with stoichiometric coefficients $[b_{ij}]$ as in

$$C_i = \sum_{j=1}^{l} b_{ij} B_j \ , \qquad \text{with } i{=}1, s; \ l{=}3; \ s{=}17 \tag{7}$$

To get matrix $[b]$ we start from $[a]$ by selecting the "l" substances selected as the new basis (B), which are nothing but a sub-vector of the vector (C), with its own sub-matrix of formation $[a_{jj}]$, namely the upper three lines in (5),

667

$$\sum_{j=1}^{l} \hat{a}_{jj} A_j = B_j \qquad\qquad j=1,s; \; l=3; \; s=17 \qquad\qquad (8)$$

In order to make the new base to appear in the equations of formation (3), we eliminate $\left(A_j\right)$ by using the resolution of (8),

$$\left(A_j\right) \equiv [\hat{a}_{jj}]^{-1}[\hat{a}_{jj}](A_j) = [\hat{a}_{jj}]^{-1}(B_j) \qquad\qquad (9)$$

Introducing the value of (A_j) from (9) into (4) and comparing this result with the form in (8) the following formula is obtained

$$[a_{ij}][\hat{a}_{jj}]^{-1} = [b_{ij}] \qquad\qquad (10)$$

First we apply the method by finding the inverse of the sub-matrix $[\hat{a}_{jj}]$ from (9), which is a standard operation as far as the sub-matrix is non-singular (non-zero determinant),

$$\Delta_{jj} = \begin{vmatrix} 2 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 2 \end{vmatrix} = 2 \neq 0 \;.$$

One obtains the inverse as

$$[\hat{a}_{jj}]^T \equiv [\hat{a}_{jj}], \qquad\qquad [\hat{a}_{jj}]^{-1} \equiv \frac{1}{\Delta}\begin{bmatrix} 2 & -2 & 0 \\ -2 & 4 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & -1 & 0 \\ -1 & 2 & 0 \\ 0 & 0 & 1/2 \end{bmatrix} \qquad (11)$$

The proof shows that $[\hat{a}_{jj}]^{-1}[\hat{a}_{jj}] = [E]$. With formula (10) the dissociation of the products into the new basis results as

$$
\begin{array}{ccc}
O & C & H
\end{array}
\qquad\qquad
\begin{array}{ccc}
CO_2 & CO & H_2
\end{array}
$$

$$
\begin{bmatrix}
2 & 1 & 0 \\
1 & 1 & 0 \\
0 & 0 & 2 \\
1 & 0 & 2 \\
1 & 0 & 1 \\
1 & 1 & 1 \\
1 & 1 & 2 \\
2 & 0 & 2 \\
2 & 0 & 1 \\
0 & 1 & 3 \\
1 & 2 & 0 \\
0 & 1 & 2 \\
0 & 1 & 4 \\
0 & 2 & 4 \\
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
1 & -1 & 0 \\
-1 & 2 & 0 \\
0 & 0 & 1/2
\end{bmatrix}
=
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1 \\
1 & -1 & 1 \\
1 & -1 & 1/2 \\
0 & 1 & 1/2 \\
0 & 1 & 1 \\
2 & -2 & 1 \\
2 & -2 & 1/2 \\
-1 & 2 & 3/2 \\
-1 & 3 & 0 \\
-1 & 2 & 1 \\
-1 & 2 & 2 \\
-2 & 4 & 2 \\
1 & -1 & 0 \\
-1 & 2 & 0 \\
0 & 0 & 1/2
\end{bmatrix}
\begin{array}{l}
CO_2 = new\ basis \\
CO = new\ basis \\
H_2 = new\ basis \\
H_2O = CO_2 - CO + H_2 \\
HO = CO_2 - CO + 1/2H_2 \\
HCO = CO + 1/2H_2 \\
CH_2O = CO + H_2 \\
H_2O_2 = 2CO_2 - 2CO + H_2 \\
HO_2 = 2CO_2 - 2CO + 1/2H_2 \\
CH_3 = 2CO - CO_2 + 3/2H_2 \\
C_2O = 3CO - CO_2 \\
CH_2 = 2CO - CO_2 + H_2 \\
CH_4 = 2CO - CO_2 + 2H_2 \\
C_2H_4 = 4CO - 2CO_2 + 2H_2 \\
O = CO_2 - CO \\
C = 2CO - CO_2 \\
H = 1/2H_2
\end{array}
\qquad (12)
$$

The same matrix [b] will be used to further calculate the equilibrium constants of dissociation of all products into the new base and to write the equations of chemical dissociation (12) involving those constants.

668

3. CONSTANTS OD DISSOCIATION INTO NON-ATOMIC BASES

According to the quantitative expression of the chemical equilibrium established between s reacting species, the constants of equilibrium derive from the variation of the *Gibbs* free energy along the considered reaction i in the form [19]

$$\ln K_i(T) \equiv -\frac{\Delta G_i^0(T)}{R_0 T}, \tag{13}$$

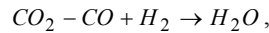where the variation of the free energy is given by

$$\Delta G_i^0 \equiv G_i^0(products) - G_i^0(initials) = \sum_{j=1}^{s} b_{ij}\left[H_j^0(T) - TS_j^0(T)\right]\Big| i = \overline{1, s-\ell}. \tag{14}$$

For all combustion products involved (3), values for enthalpy and entropy at any temperature between zero and 6000ºK are accessible through high degree polynomial regression, with accuracy of below 5ºK on the entire temperature scale [9], [18]. Using the source [18], where the polynomial coefficients match to the reduced temperature θ in thousands of degrees K, these functions are rebuilt as

$$H_j^0(T) = a_{Hj} + \sum_{k=1}^{m} a_{kj}\theta^k. \tag{15}$$

$$S_j^0(T) = a_{Sj} + a_{1j}\ln\theta + \sum_{k=2}^{n}\frac{k}{k-1}a_{kj}\theta^{k-1}. \tag{16}$$

The water-gas reaction (6), for example, usually written for the formation of water,

$$CO_2 - CO + H_2 \rightarrow H_2O,$$

performs with a variation of the free energy (14) given by

$$\Delta G_{H_2O}^0(T) = G_{H_2O}^0(T) - G_{CO_2}^0(T) + G_{CO}^0(T) - G_{H_2}^0(T), \tag{17}$$

namely

$$\Delta G_{H_2O}^0(T) = [H_{CO_2}^0(T) - TS_{CO_2}^0(T)] - [H_{CO}^0(T) - TS_{CO}^0(T)] + [H_{H_2}^0(T) - TS_{H_2}^0(T)] - $$
$$- [H_{H_2O}^0(T) - TS_{H_2O}^0(T)] \tag{18}$$

Based on the seven-degree polynomial approximations in [18], the above relation (18) gives the value of free energy variation of water-gas reaction at 2500K in kJ/mol as

$$\Delta G_{H_2O}^0(T) = -1078.2425\,3 + 702.40258 - 419.83224 + 833.78968 = 38.11749 \tag{19}$$

Using the value 8.315472 J/mol·K for the universal constant of perfect gases R_0 [21], the equilibrium constant as given in (14) results

$$\ln K_{H_2O}(2500) = -1.8335695 \qquad K_{H_2O}(2500) = 1/6.2561784 \equiv 0.1598420 \tag{20}$$

All the other constants are calculated with the same rule using the stoichiometric coefficients b_{ij} of formation from the new basis.

4. EQUILIBRIUM COMBUSTION AT p, $T=const$.

The combustion process of a solid propellant grain or of vaporized liquid mixture passes through complex chemical transforms, including violent exothermal reactions between active radicals that last for extremely short time intervals. The extent and details of intermediate reactions are almost impossible to observe experimentally and they only are imagined as more or less realistic models. After all those intermediate changes are finished however, the steady state of the combustion products may be resolved more accurate, from the energy and material balance of the whole process and this is the exact target of thermochemical computations of the combustion process.

Assuming that the final products of combustion behave in chemical equilibrium after completing isobaric combustion of a propellant P, with given chemical composition

$$P \equiv A_O A_C A_H ,\tag{21}$$

where A_i is the number of gram-atoms of each chemical element i from the system, the equations that describe the final state of the combustion products are the following:

4.1. Equations of chemical equilibrium

The equations of chemical equilibrium are those that accompany the s-l formation-dissociation processes given in (7) and detailed in (12) and link the partial pressures as

$$K_i(T) = \prod_{j=1}^{l} (p_j)^{b_{ij}} \quad | i = 1, s - l .\tag{22}$$

4.2. Equations of element conservation

For the l chemical elements that form the propellant an equal number of mass conservation equations must be satisfied, namely

$$A_i = \sum_{j=1}^{s} a_{ij} n_j \quad | i = s - l, s .\tag{23}$$

They are written through the number of moles n_j of each species that appears into one kg of mixture. They are immediately recast through partial pressures when the proportionality law between the number of moles and the total number of gas moles on one hand and the partial pressure and the total pressure on the other is considered,

$$A_i \frac{p_\Sigma}{n_G} = \sum_{j=1}^{s} a_{ij} p_j \quad | i = s - l, s .\tag{24}$$

The unknown total number of gaseous moles n_G appears as a new variable for which the Dalton sum of pressures supplements the system with one equation.

4.3. Dalton equation

The sum of all s partial pressures is the total static pressure of the gaseous mixture,

$$p_\Sigma = \sum_{j=1}^{s} p_j .\tag{25}$$

4.4. Conservation of enthalpy

The individual total standard enthalpy for each substance H^0_j at the indicated temperature T is added after weighing with the number of moles n_j to render the enthalpy of the mixture. This total enthalpy of the mixture must equal the enthalpy of the initial propellant H_p when no heat losses are encountered and serves as the extra equation for the unknown temperature of the gas mixture,

$$H_p = \sum_{j=1}^{s} n_j H^0_j(T) = \frac{n_G}{p_\Sigma} \sum_{j=1}^{s} p_j H^0_j(T) .\tag{26}$$

The above $s+2$ equations allow computing the s chemical concentrations plus the total number of moles of different gases into a unit mass of propellant n_G and the temperature of the gases T_c at the given total pressure p_Σ. It is a problem of numerical computation to solve this nonlinear algebraic system (22)-(26) and a lot of methods had been employed during the time to accomplish this thermochemical computation. The so-called general methods offer universal solving procedures, well adapted for electronic computing. The method previously developed at the chair in UPB is a direct linearization way to compute corrections to species concentration and to the number of moles through an iterating procedure. It proved very intuitive and useful for didactic purposes, while its convergence speed equals that of all the other top efficient methods.

5. NUMERICAL RESULTS

Investigations were performed over the chemical propellant with liquid oxigen as oxidizer and unsymmetrical dimethylhydrazine as the fuel. The numerical code gives confident results, in good agreement with other thermochemical codes previously developed [20].
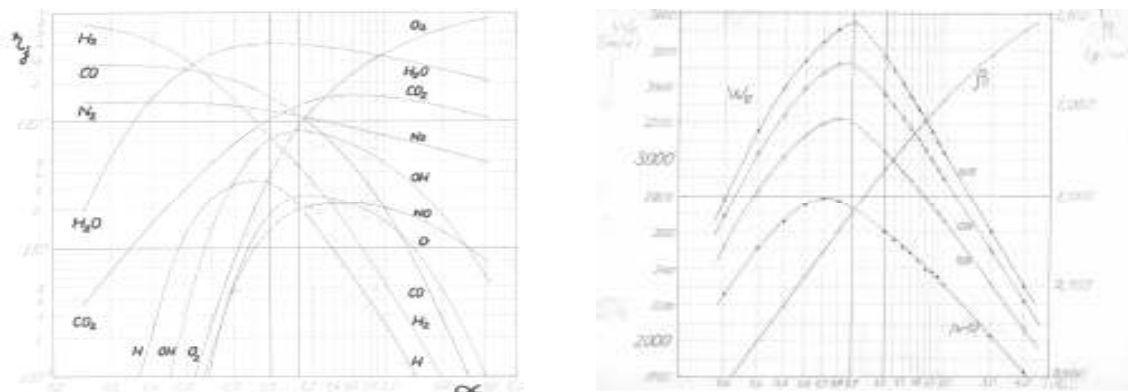

Figure 1. Combustion products, exit velocity and bulk density vs. oxidizer excess.

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