J. Serb. Chem. Soc. 65(11)803–810(2000)
JSCS–2807

UDC 662.3/.311.1/.312
Original scientific paper

Calculation of complex chemical equilibrium compositions of composite rocket propellants combustion products

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(Received 12 May, revised 3 July 2000)

An adequate method for calculating chemical equilibrium in a predominantly gaseous, multi-component reactive mixture was investigated and successfully applied. This method involves the stated equilibrium reaction scheme, including, first, the formation of chemical species, of which concentrations prevail in the mixture, then the formation of gaseous atomic species by dissociation of previous ones, and, finally, the formation of complex chemical species from the atomic species. A computer program, which permits calculations of equilibrium compositions by the iteration procedure, has been developed. The results of calculations have been compared with data obtained by the programs OPHELIE, MICROPEP, and the program SPP, as documented in the NASA-Lewis Code, which is presently the world-wide standard. All comparisons gave satisfactory agreement.

Keywords: composite propellants, combustion, combustion products, chemical equilibrium.

INTRODUCTION

The knowledge of chemical equilibrium compositions of a solid rocket propellant combustion products mixture permits the calculation of theoretical thermodynamic properties for this chemical system. These properties can be applied to a wide variety of problems in the rocket science. Some applications are the design and analysis of performance characteristics of propellant systems, combustion chambers, nozzles, and engines.

Considerable numerical calculations are necessary to obtain equilibrium compositions for complex chemical systems. For example, to calculate the flame temperature for the combustion of a hydrocarbon in air, it might be necessary to consider as many as 20 or more chemical reactions.[1] As the number of reactions increases, so does the mathematical difficulty. Simultaneous equilibrium constants relations can no longer be solved in a closed form, even approximately. It becomes necessary to use either trial and error or an iterative approach to obtain solutions of the system of simultaneous equations.

Several different approaches have been used to obtain solutions of the system of simultaneous equations describing chemical equilibra.[1–7] Some of the calculation

methods were designed for specific problems and often took advantage of some special characteristic of the particular problem to facilitate its solution. Other methods were intended to be multipurpose schemes that could, at least in principle, be applied to any chemical equilibrium problem.

The aim of this work was to find a more general and consistent, but simple method for the calculation of chemical equilibrium compositions of the combustion products of composite propellants.

DESCRIPTION OF THE MODEL

In general, gaseous atomic species, gaseous complex chemical species (some of them can simultaneously exist in the condensed phase), and condensed chemical species can coexist in the combustion products of solid propellans. In this paper, the ionized species are not considered.

The most probable chemical species which can be formed from the atoms of the propellants and which can exist in the conditions of combustion have to be known or postulated.

It is assumed[1–6] that the equation of state for an ideal gas can be applied for the combustion products mixture, even when small amounts of condensed species (up to several percents by mass) are present.

Chemical equilibrium is described by the equilibrium constants formulation. This formulation involves non-linear equations of chemical equilibria among combustion products and linear mass-balance equations:

$$\sum_{j=1}^{NP} a_{ij} n_j - x_i = 0; \qquad i = 1,2,..., NEL \tag{1}$$

where x_i is the coefficient in the specific formula of a propellant for the element X^i, a_{ij} is the number of atoms of the element X^i in the combustion product j (coefficients in molecular formula of the combustion product j), n_j is the number of moles of the j^{th} combustion product in the mass unit of the combustion product mixture, NP is the total number of chemical species in the combustion products, and NEL is the total number of chemical elements in a propellant.

When the constituents of a propellant are defined by their molecular formulas, the coefficients of the propellant specific formula can be calculated using the following set of equations:

$$x_i = 0.01 \sum_{k=1}^{NP} \frac{q_k \nu_{ik}}{M_k}; \qquad i = 1,2,..., NEL \tag{2}$$

where q_k is the mass percent of constituent k in a propellant, ν_{ik} is the number of atoms of the element i in the constituent k (coefficients in the molecular formula of the constituent k), M_k is the molar mass of the constituent k, NK is the number of constituents in a propellant.

For the general reaction: $\sum_k a_k A_k \leftrightarrows \sum_l b_l B_l$, where a_k and b_l are the stoichiometric molar coefficients of the chemical molecules (or atoms) of the reactants A_k and the products B_l, respectively, the equilibrium constant equation can be expressed as:

$$K_p = \frac{\prod_l \left(n_{B_l}\right)^{b_l}}{\prod_k \left(n_{A_k}\right)^{a_k}} \left(\frac{p}{n\,p_0}\right)^{\sum_l b_l - \sum_k a_k} \tag{3}$$

where K_p is the equilibrium constant and the n_{B_l} and n_{A_k} are the number of moles of the reactants A_k and products B_l, p is the actual pressure at which the reaction occurs, and p_0 is the reference pressure.

The values of K_p for this general reaction can be calculated using the following equation:

$$\ln K_p(T) = \frac{1}{R}\left[\sum_l b_l s(p_0,T)_{B_l} - \sum_k a_k s(p_0,T)_{A_k}\right] - \\ - \frac{1}{RT}\left[\sum_l b_l h(p_0,T)_{B_l} - \sum_k a_k h(p_0,T)_{A_k}\right] \tag{4}$$

where $s(p_0, T)$ and $h(p_0, T)$ are the molar entropy and the total molar enthalpy under standard conditions for the reactants and products, and R is the gas constant.

The mass balance equations (Eq. 1) and the equilibrium constants equations (Eq. 3) permit the determination of equilibrium compositions for the thermodynamic states specified by the assigned temperature and pressure.

The thermodynamic functions of the combustion products, being in their standard state, are obtainable from the JANAF thermodynamic tables.[8] For each combustion product (subscript j), the total molar enthalpy is given in the form of least squares coefficients as follows:

$$h_j^0(T) = c_{0,j} + \sum_{i=1}^{6} c_{i,j}\ (10^{-3}T)^i \tag{5}$$

where c_0 and c_i are the least squares coefficients, and i denotes the degree of the polynomial.

The molar entropy is determined as:

$$s_j^0(T) = c_{s,j} + 10^{-3}\, c_{1,j} \ln(10^{-3}\, T) + 10^{-3} \sum_{i=2}^{6} \frac{i}{i-1} c_{i,j} (10^{-3}\, T)^{i-1} \tag{6}$$

where the term $c_{s,j}$ is defined as the mean arithmetic value of all $c_{s,j,T}$:

$$c_{s,j,T} = s_j^0(T_{tab}) - 10^{-3}\, c_{1,j} \ln(10^{-3}\, T_{tab}) - 10^{-3} \sum_{i=2}^{6} \frac{i}{i-1} c_{i,j} (10^{-3}\, T_{tab})^{i-1} \tag{7}$$

where T_{tab} and $s_j^0(T_{tab})$ are the any data pair from the tabulated thermochemical data.[8]

Sixth-order polynomials have been used to approximate the data for gaseous species over two temperature ranges (from 298.15 to 1000 K, and from 1000 to 6000 K), and fourth-order polynomials for condensed species over a specified temperature range. The accuracy of approximation has been estimated and compared with other available literature data.[9,11] The absolute errors of the temperature were always lower than 0.5 K for each combustion product. These absolute errors of temperature are much lower than the acceptance criterion defined as $|\Delta T| \leq 3$ (Ref. 6). It is shown that the accuracy of the approximation is improved. The polynomials coefficients are available from the authors upon request.

A typical composite rocket propellant contains C, H. N, O, Cl and Al as constitutive chemical elements. Hence, the combustion products consist of the given six elements or contain them in a bound form, and it is possible that there are more than 70 species in this reactive mixture.[2–4,12–14]

Although there are no serious difficulties in analyzing such reactive systems with, for example, more than 70 chemical species, except, perhaps, the availability of thermodynamic data for some of the components of the mixture, it is assumed in this paper that the combustion products consist of 47 components, which are presented in Table I.

TABLE I. Components of the combustion products of the composite propellants

H_2	H_2O	H	OH	O	O_2	N_2	NO	N	NH	NH_2	NH_3
N_2O	NO_2	CO_2	CO	C	HCO	HCN	CH	CH_2	CH_3	CH_4	C_2H_2
HCl	Cl	Cl_2	ClO	ClO_2	Cl_2O	CClO	CCl	CCl_2	CCl_3	CCl_4	$Al_2O_{3(l)}$
$Al_2O_{3(s)}$	Al	AlO	Al_2O	AlO_2	AlOCl	AlCl	$AlCl_2$	$AlCl_3$	AlH	AlOH	AlO_2H

In this case, all the products are gaseous except Al_2O_3 (the chamber reaction gases contain liquid aluminium oxide and the colder gases in the nozzle exhaust contain solid, condensed aluminium oxide particles).

The developed method for calculation the chemical equilibrium in such a predominantly gaseous, multi-component reactive mixture, involves the stated equilibrium reaction scheme, including, first, the formation of the major chemical species, of which concentrations prevail in the mixture, then the formation of gaseous atomic species by dissociation of the initial ones,and finally, the formation of complex chemical species from the atomic species.

As experience and calculations confirmed,[12–15] carbon dioxide, carbon monoxide, water, hydrogen, nitrogen, hydrochloric acid and aluminium oxide are the major combustion products.

The mass balance equations and the equilibrium constant of the water gas reaction are used for calculation the concentrations of the main combustions products.

Gaseous atomic species, according to the stated reaction scheme, are calculated from the equilibrium constants corresponding to their reactions of formation from the main combustion products and the other complex chemical species are obtained from the equilibrium constants corresponding to their formation from the gaseous atomic

species. If in such a thermodynamic equilibrium system at the assigned temperature, any species coexists in the gaseous and condesend phases, the partial pressure of the gaseous phase must be equal to the vapor pressure of the condensed phase of this species. This permits the determination of the amount of possibly present condensed phase in the combustion products.

The equilibrium reaction scheme, repressnting the formation of secondary combustion products is given in Table II. It yields the obligatory stoichiometric coefficients a_k and b_l for the equilibrium calculation.

This iterative procedure is continued until convergence is obtained:

$$\left| \frac{n_j^{I-1} - n_j^I}{n_j^I} \right| \leq \varepsilon$$

where I denotes the number of the I^{th} iteration, and ε is the acceptance criterion. For this type of chemical equilibria calculation, 0.00001 is the recommended value for the acceptance criterion. The convergence rate of the applied calculation method is very high.

TABLE II. Reaction scheme for the formation of secondary combustion products

$2CO \leftrightarrow CO_2+C$	$0.5H_2 \leftrightarrow H$	$H_2O \leftrightarrow H_2+O$	$0.5N_2 \leftrightarrow N$	$HCl \leftrightarrow H+Cl$	$Al_2O_{3(con)} \leftrightarrow 2Al+3O$
$H+O \leftrightarrow HO$	$N+O \leftrightarrow NO$	$2O \leftrightarrow O_2$	$H+C+O \leftrightarrow HCO$	$H+C+N \leftrightarrow HCN$	$C+H \leftrightarrow CH$
$C+2H \leftrightarrow CH_2$	$C+3H \leftrightarrow CH_3$	$C+4H \leftrightarrow CH_4$	$2C+2H \leftrightarrow C_2H_2$	$N+H \leftrightarrow NH$	$N+2H \leftrightarrow NH_2$
$N+3H \leftrightarrow NH_3$	$2N+O \leftrightarrow N_2O$	$N+2O \leftrightarrow NO_2$	$2Cl \leftrightarrow Cl_2$	$Cl+O \leftrightarrow ClO$	$Cl+2O \leftrightarrow ClO_2$
$2Cl+O \leftrightarrow Cl_2O$	$C+Cl+O \leftrightarrow CClO$	$C+Cl \leftrightarrow CCl$	$C+2Cl \leftrightarrow CCl_2$	$C+3Cl \leftrightarrow CCl_3$	$C+4Cl \leftrightarrow CCl_4$
$Al+O \leftrightarrow AlO$	$2Al+O \leftrightarrow Al_2O$	$Al+2O \leftrightarrow AlO_2$	$Al+Cl+O \leftrightarrow AlClO$	$Al+Cl \leftrightarrow AlCl$	$Al+2Cl \leftrightarrow AlCl_2$
$Al+3Cl \leftrightarrow AlCl_3$	$Al+H \leftrightarrow AlH$	$Al+O+H \leftrightarrow AlOH$	$Al+2O+H \leftrightarrow AlO_2H$		

RESULTS AND DISCUSSION

A computer program, named CEC (Chemical Equilibrium Calculation), has been developed on the basis of the above-mentioned algorithm. The CEC program is a PC-based computer code and is assigned for 32-bit Windows environment. It is written in Visual Basic as the programming language.

Numerous results of these calculations were obtained for different composite propellant formulations and rocket motor conditions. Only one example is indicated here to illustrate typical values of the combustion products compositions that characterize different locations in a rocket motor for aluminized composite propellants, and to compare the calculated values with corresponding available values obtained by the OPHELIE program,[14] currently in use. Namely, the successful verification of the presented method and the CEC program has been conceived to give an affirmative answer with respect to the results of this computer code and some others programs, which are presently world-wide standards.

The results of these calculations and the corresponding comparative analysis are presented in Table III.

TABLE III. Comparative analyses of the calculated mole fractions of the combustion products obtained by various computer codes for the propellant AP/Al/ 70/16/14

Program	OPHELIE	CEC		OPHELIE	CEC		OPHELIE	CEC	
Section	Chamber			Throat			Exit		
T/K	3315			3101			1541		
P/bar	70.9275			40.6700			0.2432		
Products	mol/%	mol/%	Diff./%	mol/%	mol/%	Diff./%	mol/%	mol/%	Diff./%
H_2	29.107	29.116	–0.03	29.572	29.578	–0.02	32.156	32.162	–0.02
H_2O	13.704	13.696	0.06	13.548	13.539	0.06	11.923	11.917	0.05
H	2.347	2.346	0.04	1.750	1.752	–0.11	0.003	0.003	0.00
OH	0.465	0.463	0.43	0.291	0.290	0.34		3.767×10^{-5}	
O	0.022	0.022	0.00	0.011	0.011	0.00			
O_2	0.004	0.004	0.00	0.002	0.002	0.00			
N_2	7.582	7.581	0.01	7.623	7.622	0.01	7.726	7.725	0.02
NO	0.031	0.030	3.23	0.017	0.017	0.00			
N		2.732×10^{-4}			1.077×10^{-4}				
NH	0.001	0.001	0.00		3.244×10^{-4}				
NH_2	0.001	0.001	0.00	0.001	0.001	0.00			
NH_3	0.002	0.002	0.00	0.001	0.001	0.00		7.181×10^{-5}	
CO_2	1.414	1.409	0.35	1.445	1.440	0.34	2.991	2.984	0.23
CO	23.214	23.223	–0.04	23.296	23.305	–0.04	22.062	22.073	–0.05
HCO	0.016	0.016	0.00	0.010	0.010	0.00		1.719×10^{-5}	
HCN	0.001	0.001	0.00	0.001	1.000×10^{-3}	0.00			
HCl	13.402	13.407	–0.04	14.039	14.040	–0.01	15.447	15.445	0.02
Cl	0.730	0.727	0.41	0.568	0.567	0.18	0.001	0.001	0.00
Cl_2	0.002	0.002	0.00	0.001	0.001	0.00			
ClO		3.271×10^{-4}			1.407×10^{-4}				
CClO		9.912×10^{-4}			5.402×10^{-4}				
$Al_2O_{3(l)}$	7.174	7.176	–0.03	7.369	7.369	0.00			
$Al_2O_{3(s)}$							7.688	7.686	0.02
Al	0.004	0.004	0.00	0.001	0.001	0.00			
AlO	0.004	0.004	0.00	0.001	0.001	0.00			
Al_2O	0.001	0.001	0.00	0.000	0.000				
AlO_2	0.001	0.001	0.00		2.744×10^{-4}				
AlOCl	0.092	0.091	1.09	0.052	0.052	0.00			
AlCl	0.277	0.276	0.36	0.150	0.150	0.00			
$AlCl_2$	0.319	0.317	0.63	0.205	0.204	0.30			
$AlCl_3$	0.018	0.018	0.00	0.014	0.014	0.00		1.391×10^{-5}	
AlH	0.001	0.001	0.00		0.000				
AlOH	0.024	0.024	0.00	0.011	0.011	0.00			
AlO_2H	0.035	0.034	2.86	0.017	0.017	0.00			

Remark: Combustion products with concentrations less then 10^{-5}, are not printed.

As it can be seen from this Table, there is good agreement between the corresponding concentrations of the combustion products obtained by using various computer codes. Furthermore, it can be seen from the given Table, that the total concentrations of the major combustion products are higher than 95.0 mol % for aluminized composite propellants with a high content of aluminium in the combustion chamber, but higher than 99.9 mol % in the considered nozzle exit. Namely, the dissociation of the main combustion products increases as the temperature rises and decreases with increasing pressure. Some unreacted O_2 remains at high combustion temperatures. As the gases are cooled in the nozzle expansion, the dissociated species react again to form molecules. Hence, only a small percentage of the dissociated species persits at the nozzle exit and only with the high content of oxidizer, where the exit temperature is relatively high. This fact confirms the validity of the accepted iteration method for the calculation of complex chemical equilibrium concentrations for conventional composite propellants.

Other comparisons with respect to the MICROPEP[13] and SPP[15] programs gave satisfactory agreement, as well.

Although in the analysis of the chemical ingredients of these solid propellants, approximately 70 additional reaction products were considered in addition to the major product species in the French program, named OPHELIE, their calculated mole fractions were very small and therefore they have been neglected, and are not included in Table III. This means that our computer code CEC, which analyzes 47 combustion products, is very suitable for this type of propellant. Contrary to other analyzed programs, the CEC computer code is assigned to extensive calculations on a particular chemical system – typical composite propellants.

CONCLUSION

An adequate method and a computer program for the calculation of chemical equilibrium in the combustion products of composite propellants have been developed, and are successfully verified. The results of the calculations have been compared with data obtained by other programs, which are presently world-wide standards. All the comparisons gave satisfactory agreement.

ИЗВОД

ПРОРАЧУН СЛОЖЕНИХ ХЕМИЈСКИХ РАВНОТЕЖНИХ САСТАВА ПРОДУКАТА САГОРЕВАЊА КОМПОЗИТНИХ РАКЕТНИХ ГОРИВА

МИЛОШ ФИЛИПОВИЋ и НИКОЛА КИЛИБАРДА

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Истраживан је и успешно доказан метод прорачуна хемијске равнотеже у претежно гасовитој, вишекомпонентној реактивној смеши. Овај метод обухвата формулисану реакциону схему, која укључује стварање хемијских врста чије концентрације преовлађују у смеши у првом кораку, затим стварање гасовитих атомских врста дисоцијацијом претходних и, на крају, стварање сложених хемијских врста из атомских гасовитих врста. Развијен је рачунарски програм који омогућава прорачун равнотежних састава. Резултати прора-

чуна компарирани су са подацима добијеним коришћењем програма OPHELIE, MICROPEP и програма SPP, документованог у NASA-Lewis Code-у, који представља светски стандард. Сва поређења дала су задовољавајуће слагање резултата.

(Примљено 12. маја, ревидирано 3. јула 2000)

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