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Research paper

Calculation of the Thermochemical Parameters of High-Temperature Pyrolants

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Abstract: The thermochemical properties of high-temperature pyrolants were studied. Two reactive oxidizers, potassium nitrate (KNO_3) and potassium perchlorate ($KClO_4$), and two highly energetic fuels, boron (B) and zirconium (Zr), were considered. The combustion temperatures and thermochemical parameters of B/KNO_3, Zr/KNO_3, B/$KClO_4$, and Zr/$KClO_4$ pyrotechnic mixtures were investigated *via* thermochemical calculations using a modified dedicated calculation program package that enables estimation of the presence and concentrations of chemical compounds in condensed (solid or liquid) phases in the combustion products. The relevancy between heat generation and the quantity of gaseous and condensed products was calculated. In addition, changes in the thermochemical parameters of the pyrotechnic mixtures on increasing the combustion pressure from 0.4 to 4.0 MPa were examined. The use of zirconium led to remarkably higher combustion product temperatures compared with other metallic fuels.

Keywords: high-temperature pyrolants, thermochemical parameters, computer calculation program

Symbols and abbreviations

T	temperature [K]
p	pressure [Pa]
n_g	total number of compounds in gaseous phase
n_s	total number of compounds in condensed (liquid or solid) phases

m	number of elements present in the mixture
$\Delta_f H_i$(298.15K)	formation enthalpy of species "i" at 298.15 K
Q_c	heat of combustion
B_T	oxygen balance [%]
$\Sigma y_i^{(g)}$	total number of moles of gaseous components
V_{gas}	total volume of substances in gaseous phase (per unit mass)

1 Introduction

Igniters fulfill an essential function in rocket motors and pyrotechnic devices. Their purpose is to initiate the stable combustion of a propelling charge situated inside a rocket chamber equipped with one or more nozzles of specified geometrical dimensions. During the stable operation of a rocket motor, a thermodynamic balance exists between the high-temperature gaseous products from the propellant and their outflow through the nozzle. Owing to this balance, the pressure inside a rocket chamber is stable or changes slowly, indicating the correct design and performance of the entire propulsion system. Any mechanical defects in the propellant charge or physical or chemical instabilities of the propellant can cause unstable combustion, which usually results in explosion of the rocket motor [1-5]. An unstable combustion stage also occurs at the moment of ignition of the propelling charge by the igniter. Following ignition, the pressure inside the rocket chamber increases from atmospheric level to the nominal value and stabilizes in a very short time, which is of the order of tenths of a second.

Traditional igniters consist of a precisely determined quantity of granular black powder, which serves as a source of hot gases that initiate combustion of the exposed surfaces of the propelling charge. The combustion products of black powder also include significant amounts of high-temperature solid particles, which initiate the combustion of the propellant more efficiently than the hot gases. The mass of the initiation charge has been verified experimentally for the entire range of operation temperatures. This range is typically from −50 to +70 °C. The temperature exerts a significant influence on the combustion kinetics of both the black powder in the igniter and the propellant (especially double-base propellants), which has motivated the search for other methods for igniting military rocket motors [6-9].

Five decades ago a new method for igniting the propelling charges in rocket motors was proposed [10, 11]. This method relies on replacing the black powder with a low-gaseous pyrotechnic composition (pyrolant) possessing a very high heat of combustion. The temperature of the solid combustion products

from these pyrolants typically reaches 3000 K [12-17]. This eliminates some of the hazards associated with traditional igniters, such as the additional increase in the pressure inside the rocket chamber due to the gases from the black powder combustion. Consequently, the pressure increase inside the rocket chamber originates mainly from the combustion of the propellant, which reduces the probability of the pressure exceeding the safe limit. The very high temperature of the solid combustion products of pyrotechnic mixtures ensures high ignition efficiency for the exposed surfaces of the propellant over a wide range of exploitation temperatures.

In the present study, the combustion products of two types of pyrotechnic mixtures with various compositions were investigated. Two reactive oxidizers, potassium nitrate (KNO_3) and potassium perchlorate ($KClO_4$), and two high-energy fuels, boron (B) and zirconium (Zr), were considered. The combustion temperature and thermochemical parameters of B/KNO_3, Zr/KNO_3, B/$KClO_4$, and Zr/$KClO_4$ mixtures were investigated. An improved method for identifying the presence and concentration of combustion products in condensed phases was adopted. In addition, in order to evaluate the influence of pressure on the expansion of the combustion products, the variation of the combustion energy, temperature, and concentrations of the combustion products in the gaseous and condensed phases on increasing the combustion pressure from 0.4 to 4 MPa was analyzed.

2 Method of Thermochemical Calculations

To estimate the chemical compositions and thermochemical parameters of the combustion products of the pyrotechnic mixtures, a method based on the principle of minimization of the thermodynamic potential of reactive mixtures was applied [18, 19]. The base set of equations designed to estimate the sought for concentrations of individual chemical substances that was presented in the monograph by Mader [18] is comprised of $(n_g + n_s + m + 1)$ equations, where n_g – number of substances in the gaseous phase; n_s – number of substances in the condensed, solid or liquid, phases; and m – number of elements. The improvements proposed in [19] consist of the derivation of a reduced set of $(n_s + m + 1)$ equations. The use of this reduced set simplifies the evaluation of the final composition of the reacting mixture. By solving a set of $(n_g + n_s + m + 1)$ equations, a multiplication of relatively small numbers corresponding to the gaseous species that may be present in even trace concentrations is necessary. When the reduced set is solved first, the concentrations

of n_g gaseous substances are evaluated in a simple manner [19, 20]. The inclusion into the evaluations of substances that do not contribute practically to the final composition and thermodynamic parameters may be of importance for an analysis of the possible presence of toxic substances in the combustion products. That may be of significance in the explosion of huge charges, *e.g.* in rock blasting or at shooting-ranges where same kind of munition is repeatedly employed for extended periods of time.

The possible presence of the following chemical substances that may appear in the condensed phases was considered: $B_{(s)}$, $B_2O_{3(s)}$, $BN_{(s)}$, $K_{(s)}$), $KO_{2(s)}$, $K_2O_{(s)}$, $K_2O_{2(s)}$, $KBO_{2(s)}$, $KCl_{(s)}$, $Zr_{(s)}$, and $ZrO_{2(s)}$. The concentrations of the corresponding gaseous phase components *i.e.* $B_{(g)}$, $B_{2(g)}$, $B_2O_{3(g)}$, $BN_{(g)}$, $K_{(g)}$, $K_{2(g)}$, $KO_{2(g)}$, $K_2O_{(g)}$, $K_2O_{2(g)}$, $KBO_{2(g)}$, $KCl_{(g)}$, $Zr_{(g)}$ and $ZrO_{2(g)}$ in the final composition of the combustion products was also examined. An extended list of chemical substances, such as BO, BO_2, B_2O, B_2O_2, BCl, BCl_2, BCl_3, B_2Cl_4, ClBO, Cl_2BO, and $Cl_3B_3O_3$ that may influence the combustion features of boron containing compounds [21] was included in the evaluations. Potassium compounds that are to be formed in the gaseous phase, such as KO, K_2Cl_2, KNO_2, and KNO_3, together with routine oxygen and nitrogen containing components, O, O_2, O_3, N, N_2, NO, N_2O, NO_2, N_2O_4, N_2O_3, and N_2O_5 were accounted for. The thermodynamic characteristics of the individual chemical substances were taken from thermodynamic tables [22, 23].

3 Boron-containing Compositions

3.1 B/KNO_3 compositions

The stoichiometric mixture of B/KNO_3 contains 151.26 g/kg of boron. Therefore, boron contents from 100 to 325 g/kg were considered. The dependence of the thermochemical parameters and boron azide (BN) content of the combustion products on the boron content of B/KNO_3 pyrolants is presented in Figure 1. The dependence of the available combustion volume of the studied pyrolants may occur at the quite low pressure of 0.4 MPa or at the higher pressure of 4.0 MPa. The results obtained for a pressure of 4.0 MPa are presented in Figure 2.

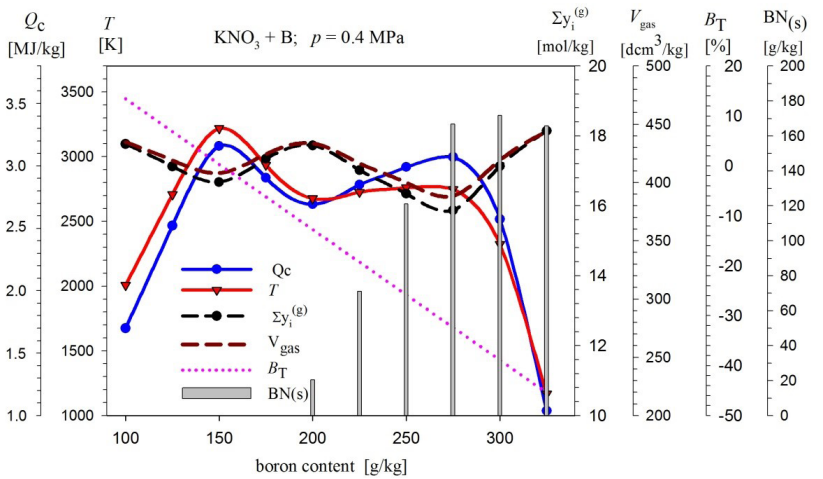

Figure 1. Dependence of the combustion energy, temperature, and quantities of gaseous and condensed products on the boron content during combustion of B/KNO_3 compositions at 0.4 MPa

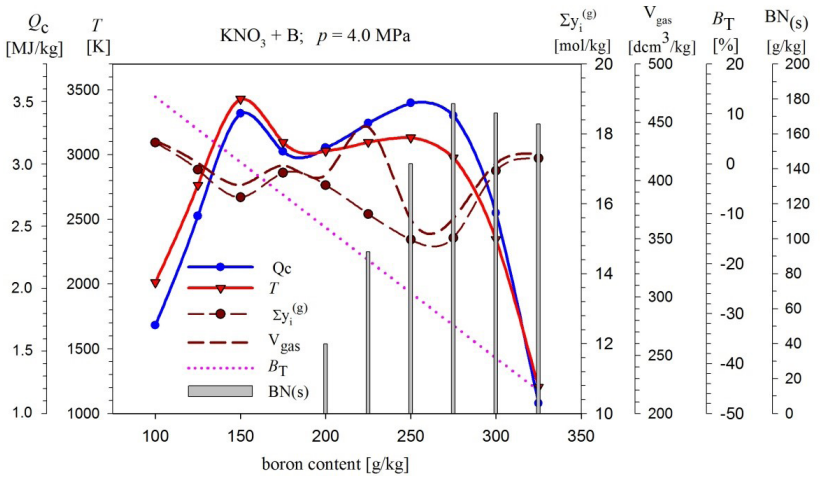

Figure 2. Dependence of the combustion energy, temperature, and quantities of gaseous and condensed products on the boron content during combustion of B/KNO_3 compositions at 4.0 MPa

The volume available to the combustion products decreases with increasing pressure. This promotes an increase in the proportion of products formed in the condensed phases. The formation of condensed-phase products,

such as $BN_{(s)}$ in the case of B/KNO_3 mixtures, causes increases in temperature and the heat of combustion (Q_c). Concomitantly, the volume of the gaseous products decreases (Figure 2). These desirable effects were observed for boron contents from 125 to 275 g/kg. In Figures 1 and 2, two particular regions of beneficial boron contents can be discerned. In comparison to the stoichiometric composition, slightly higher values of the heat of combustion were observed for boron contents in the range 125-275 g/kg. In this region, significant changes in the chemical composition of the products occurred.

The consumption of nitrogen and boron due to $BN_{(s)}$ formation leads to important changes in the final composition of the combustion products. It should be noted that B/KNO_3 mixtures with boron contents in the aforementioned range, where increases in the temperature and heat of combustion occur, are suitable for use as igniters. In both Figures 1 and 2, the heat of combustion *vs.* boron content plot displayed a second maximum at a boron content of 250-270 g/kg. This corresponds to a weaker dependence of temperature at pressures of both 0.4 and 4.0 MPa.

3.2 $B/KClO_4$ compositions

The stoichiometric mixture of $B/KClO_4$ contains 172.24 g/kg of boron. Therefore, boron contents from 100 to 275 g/kg were considered. The dependence of the thermochemical parameters of the combustion products on the boron content of $B/KClO_4$ pyrolants at pressures of 0.4 and 4.0 MPa is presented in Figures 3 and 4, respectively.

Combustion of $B/KClO_4$ mixtures does not produce products in the condensed phases. The melting point of KCl is 1044 K, but over 1800 K it sublimes. The maximal values of energy and temperature of the combustion products are attained in the vicinity of the stoichiometric composition. However, as by combustion of near-stoichiometry compositions multi-atomic molecules such as B_2O_2, B_2O_3, KBO_2 are formed in significant amounts, attaining of maximal combustion parameters is accompanied with reduction of the total molar numbers of products in the gaseous phase. An increase in combustion pressure from 0.4 to 4.0 MPa leads to a rise in temperature of the combustion products of $B/KClO_4$ pyrolants by approximately of 300 °C.

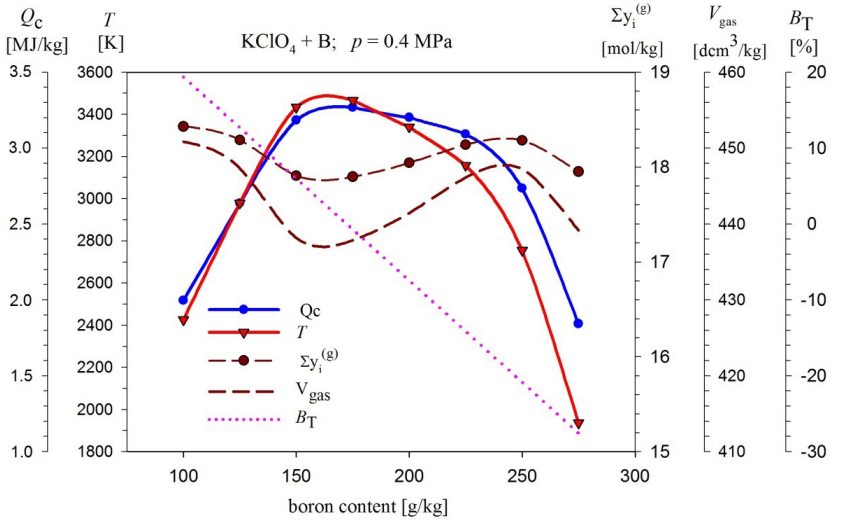

Figure 3. Dependence of the combustion energy, temperature, and quantities of gaseous and condensed products on the boron content during combustion of B/$KClO_4$ compositions at 0.4 MPa

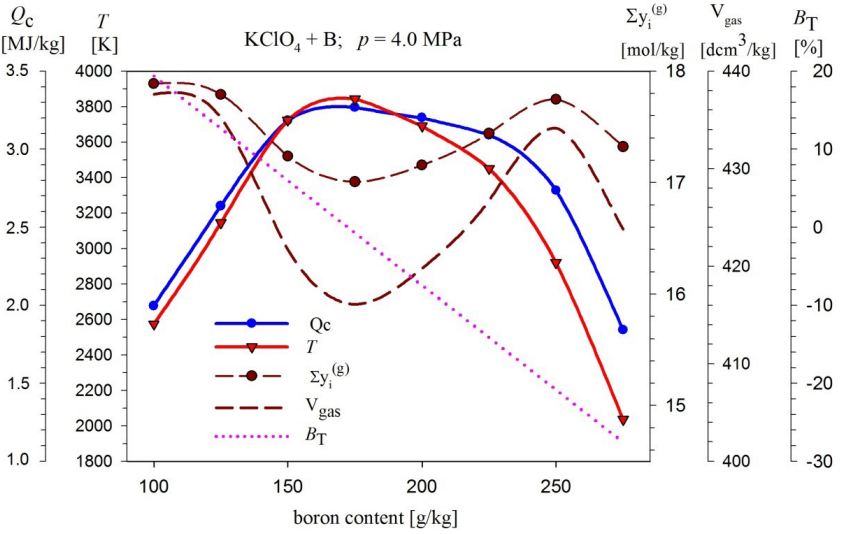

Figure 4. Dependence of the combustion energy, temperature, and quantities of gaseous and condensed products on the boron content during combustion of B/$KClO_4$ compositions at 4.0 MPa

4 Zirconium-containing Compositions

4.1 Zr/KNO_3 compositions

The stoichiometric mixture of Zr/KNO_3 contains 568.37 g/kg zirconium. Therefore, zirconium contents from 350 to 750 g/kg were considered. The dependence of the thermochemical parameters at pressures of 0.4 and 4.0 MPa is presented in Figures 5 and 6, respectively.

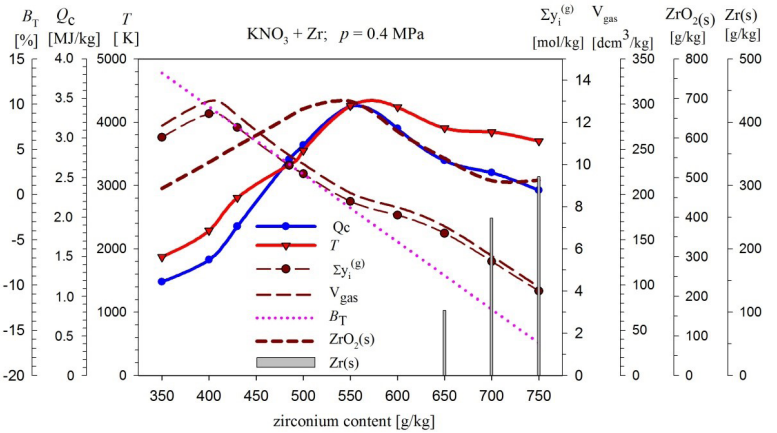

Figure 5. Dependence of the combustion energy, temperature, and quantities of gaseous and condensed products on the zirconium content during combustion of Zr/KNO_3 compositions at 0.4 MPa

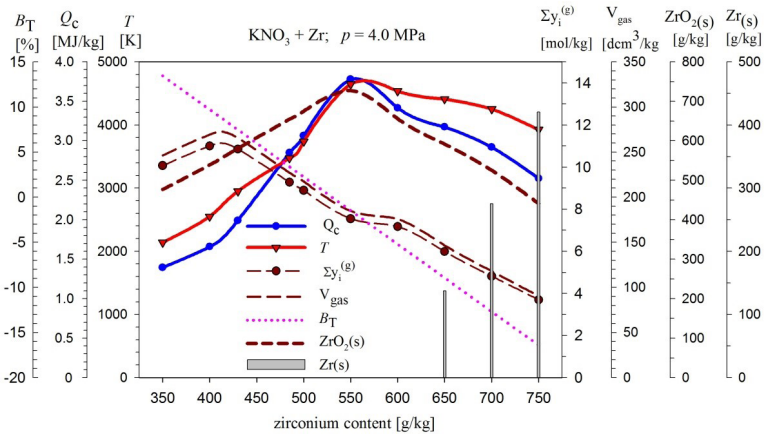

Figure 6. Dependence of the combustion energy, temperature, and quantities of gaseous and condensed products on the zirconium content during combustion of Zr/KNO_3 compositions at 4.0 MPa

The combustion of zirconium containing compositions is dominated by features derived from zirconium oxide (ZrO_2) formation. Optimal parameters are attained at Zr concentrations close to and slightly exceeding the stoichiometric mixture. The high heat of formation of $ZrO_{2(s)}$ results in temperatures and combustion energies that distinctly surpass those of mixtures based on boron. However, due to the relatively larger atomic mass of zirconium, the amount of gaseous products per unit mass is considerably smaller than in the case of boron containing mixtures. For practical use, Zr/KNO_3 mixtures with zirconium contents from 500 to even 750 g/kg may be recommended.

4.2 $Zr/KClO_4$ compositions

The stoichiometric mixture of $Zr/KClO_4$ contains 530.03 g/kg zirconium. Therefore, zirconium contents from 350 to 750 g/kg were considered. The dependence of the thermochemical parameters at pressures of 0.4 and 4.0 MPa is presented in Figures 7 and 8, respectively.

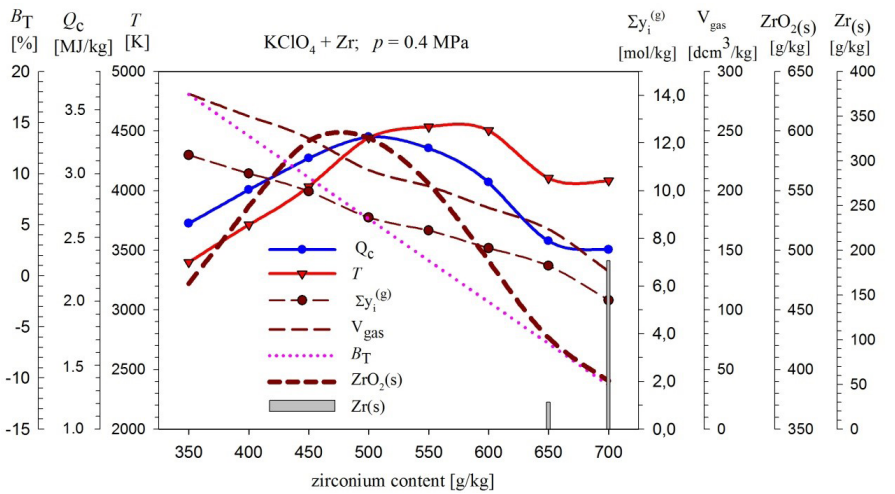

Figure 7. Dependence of the combustion energy, temperature, and quantities of gaseous and condensed products on the zirconium content during combustion of $Zr/KClO_4$ compositions at 0.4 MPa

The combustion temperature, as well as the combustion energy of $Zr/KClO_4$ mixtures exceed the values obtained for Zr/KNO_3 compositions and were the highest of the pyrolants studied. In particular, the combustion temperature for zirconium contents of 50-63% at a pressure of 4.0 MPa exceeds 5000 K.

An important factor contributing to the rise in the combustion temperature of $Zr/KClO_4$ mixtures, in comparison to Zr/KNO_3 compositions, is the formation of potassium chloride ($KCl_{(g)}$) with its negative enthalpy of formation. Another important feature of the combustion of $Zr/KClO_4$ mixtures is the significant increase in temperature that occurs on increasing the combustion pressure. An increase of pressure from 0.4 to 4.0 MPa led to a temperature rise of approximately 700 °C. The alteration in the chemical composition of $Zr/KClO_4$ combustion products on increasing the pressure from 0.4 to 4.0 MPa is listed in Table 1. The species listed are those for which the changes are greater than 0.1 mol/kg or exceed 10%.

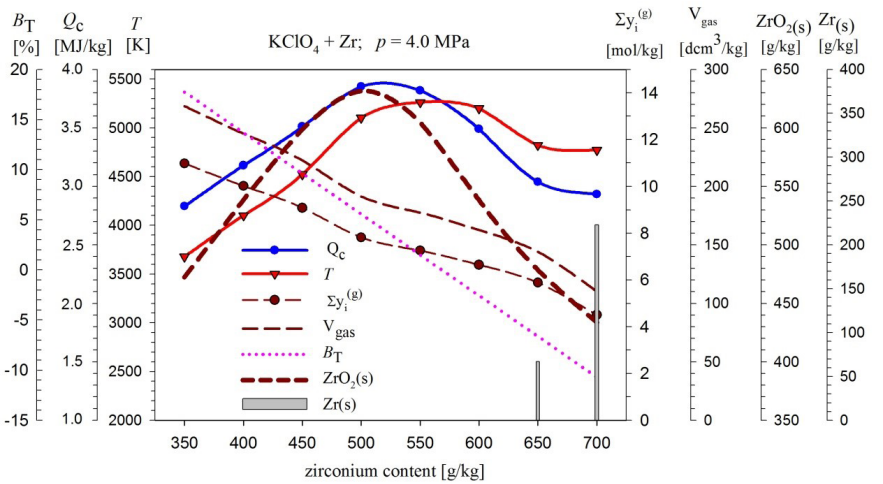

Figure 8. Dependence of the combustion energy, temperature, and quantities of gaseous and condensed products on the zirconium content during combustion of $Zr/KClO_4$ compositions at 4.0 MPa

The change in molar numbers is denoted by the symbol Δy, while the percentage alteration is listed in the final column. A noticeable alteration of concentrations of several components of combustion products may be observed. In particular, the enlargement of solid zirconium oxide ($ZrO_{2(s)}$) content contributes to increase of temperature and combustion energy. Besides, a lowering of the total amount of products in the gaseous phase ($\Sigma y_i^{(g)}$) occurs.

Table 1 Alteration of molar concentrations of illustrative components in the combustion products of a $Zr/KClO_4$ mixture caused by the increase in pressure from 0.4 to 4 MPa

Species	$\Delta_f H(298.15)$ [kJ/mol]	Δy [mol/kg]	[%]
O	249.2	–0.276	–17.4
Cl	121.3	–0.419	–22.2
$K_{(g)}$	89.0	–0.489	–26.6
$KCl_{(g)}$	–214.6	0.411	30.3
$ZrO_{(g)}$	83.9	–0.174	–19.9
$ZrO_{2(g)}$	–318.3	–0.225	–35.2
$ZrO_{2(s)}$	–1100.3	0.395	8.7
$\Sigma y_i^{(g)}$	–	–1.071	–12.9

5 Conclusions

Thermochemical calculations were performed using a modified program package that enables easier estimation of the chemical composition of the condensed (solid or liquid) phases of the combustion products. It should be stressed that in the modified method the reduced set of equations consists of six to nine equations, depending on the number of species considered in the condensed phases. Calculations were performed to evaluate the influence of the metallic fuel content in the pyrolants on the heat of combustion, temperature of the combustion products, and volume of gaseous products over a wide range of chemical compositions of the pyrotechnic mixtures.

The thermochemical properties were calculated for four types of highly energetic low-gaseous pyrotechnic mixtures. Two of the most common inorganic reactive oxidizers, potassium nitrate (KNO_3) and potassium perchlorate ($KClO_4$), and two highly energetic fuels, boron (B) and zirconium (Zr), were considered in this study. Nevertheless, the developed calculation method is also applicable to determining the thermochemical parameters and composition of combustion products for any other combination of oxidizer and fuel forming a pyrotechnic mixture.

Changes in the combustion parameters of the examined low-gaseous pyrotechnic mixtures were observed upon increasing the combustion pressure from 0.4 to 4.0 MPa. For example, increasing the pressure from 0.4 to 4.0 MPa for the $Zr/KClO_4$ pyrolants led to a significant increase (approximately 700 °C) in the temperature of the combustion products. At a pressure of 4.0 MPa,

the calculated combustion temperature of the Zr/$KClO_4$ pyrolants exceeded 5000 K over a wide range of zirconium contents (50-63%). The combustion temperatures of the studied pyrolants, based on oxygen-containing oxidizers, were significantly higher than those reported for non-oxygen-containing pyrolants, such as the Al/Mg/PTFE composition [24, 25].

The results described herein are expected to prove valuable for the selection of suitable chemical compositions for use in igniters for rocket motors and pyrotechnic devices. The practical conclusion that emerges from these calculations is the advisability of using igniters based on pyrolants that burn at higher pressures to achieve reliable ignition of rocket motors.

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