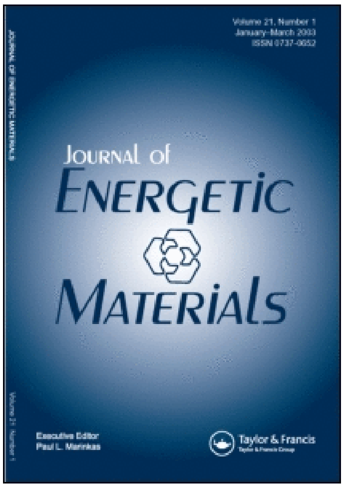

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Calculation of thermodynamic parameters of combustion products of propellants under constant volume conditions using the virial equation of state. Influence of values of virial coefficients

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CALCULATION OF THERMODYNAMIC PARAMETERS OF COMBUSTION PRODUCTS OF PROPELLANTS UNDER CONSTANT VOLUME CONDITIONS USING THE VIRIAL EQUATION OF STATE. INFLUENCE OF VALUES OF VIRIAL COEFFICIENTS

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ABSTRACT

The thermodynamic aspects of the propellant combustion under constant volume conditions are considered. The combustion model and computer program named BOMBA8 for the calculation of the thermodynamic and interior ballistics parameters of combustion products are described.

The equilibrium composition of combustion products is calculated by applying the Gibbs energy minimization method. The pressure and thermodynamic parameters of combustion products are calculated by applying the virile equation of state. The virile coefficients of individual species are calculated in different manners - applying equations derived from experimental measurements and using different potential equations.

The applicability of the presented combustion model and computer program is tested on several different types of propellants under different combustion conditions.

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INTRODUCTION

An improvement of the interior ballistics models, i.e. more accurate and more reliable theoretical calculations of propellant performances, is of ballisticians' permanent need. It is also one of the important preconditions for the development of new propellants and the designation of new high-performances guns[1].

The calculation of projectile muzzle velocity, and distribution of the chamber pressure, knowing only the loading density and propellant's composition and configuration, is the central problem of the interior ballistics. To solve this problem one has to consider a variety of mechanical, kinetic, gasdynamic, and geometric factors, as well as the thermodynamics of propellant combustion.

The thermodynamic aspects of interior ballistic problem, simplified to the propellant combustion under closed volume conditions, are considered in this paper. That includes calculation of the equilibrium composition of propellant combustion products, maximum pressure, internal energy of combustion products, specific energy, and other parameters necessary for interior ballistics calculations.

The main difficulties in performing the calculation lie in the mathematical expression of the chemical equilibrium in combustion products, then in the choice of adequate equation of state of combustion products as real gases, and in the fact that the thermodynamic functions of gaseous products at high density should be considered as functions of temperature and density[1,2,3,4,5,6].

DESCRIPTION OF THE MODEL

On the basis of the assumptions that the combustion of a propellant proceeds without heat losses to the surrounding (i.e. adiabatically), and that in the propellant combustion products the state of chemical equilibrium establishes, the algorithm and the computer program named BOMBA8 were developed. The calculations in the computer program are performed as follows:

- the state of gaseous combustion products is described by the virial equation of state[1,7],
- solid combustion products (if any) are considered as incompressible,
- the thermodynamic functions of propellant gaseous products as real gases are derived applying thermodynamics laws and virial equation of state[5,7],
- the thermodynamic functions of combustion products in the standard state are calculated from the enthalpy[8],
- the system of equations mathematically expressing the state of equilibrium in the combustion products is formed on the basis of the Gibbs energy minimization method[3,4,6,9,10],
- the system of equations is solved applying modified Newton's method[2,3,4].

Calculation of Pressure

The pressure of combustion products is calculated using the virial equation of state truncated at the third term [1,7,11,12]:

$$\frac{pV}{nRT} = 1 + \frac{nB(T)}{V} + \frac{n^2C(T)}{V^2} \qquad (1)$$

where: B(T), C(T) are the second and third virial coefficients of the gaseous mixture,

$n = \sum n_i$

V - volume occupied by the gaseous mixture.

The virial equation of state has clear physical meaning: the first term corresponds to the behavior of an ideal gas, the second terms describes the action between two molecules, and the third one considers the interaction for three molecules, and so on.

According to classical statistical mechanics, the second virial coefficient for spherically symmetric nonpolar molecules is directly related to the interaction energy ($\varphi(r)$) between a pair of molecules, by the integral [12]:

$$B(T) = \frac{2\pi N_A}{3kT} \int_0^\infty r^3 \frac{d\varphi(r)}{dr} \exp\left(-\varphi(r) / kT\right) dr \qquad (2)$$

where: N_A - Avogadro constant

k - Boltzmann constant

r - separation distance between molecules.

Different types of equations are used to express dependence of interaction energy on separation distance between a pair of molecules and their characteristics. Frequently used are the Buckingham type (so-called "Exp-Six") of potential[11], which is valid for spherical nonpolar molecules and has three parameters of intermolecular potential (α, r_m and ε), the Lennard-Jones type (so-called "6-12") of potential[13] which has two parameters of intermolecular potential (σ and ε), and the Stockmayer potential for polar molecules.

The theoretical calculation and experimental evaluation of the virial coefficients of individual species, and their incorporation into the equation of state are the subjects of numerous works[1,11,13,14,15,16,17].

However, it should be stated that only for the second virial coefficients there is a satisfactory quantitative accord between the values obtained from macroscopic p,T,V measurements and statistical mechanical theory, while for the third virial coefficients consistent data are rarely available[1].

In order to study the influence of the values of virial coefficients on the results of calculation, three different ways for calculating virial coefficients are applied in this work:

a) the equations given by Powell et al. (these equations are derived from experimental measurements)[1],

b) the Buckingham potential (using Rice-Hirschfelder data for the reduced second virial coefficient)[11],

c) the Lennard-Jones potential (using Xiong data for the reduced second virial coefficient)[12].

The values of potential parameters ($\alpha, r_m, \varepsilon/K$) used for the calculation are given in Table 1.

The third virial coefficient of individual species (C(T)), as a function of reduced temperature, is calculated from the reduced third virial coefficient [C*(T*)] applying the Hirschfelder-Curtiss relationship[12]:

$$C(T) = b_0^2\,[C*(T*)]. \qquad (3)$$

The reduced third coefficient is calculated from the second one according to the equation proposed by Xiong[12]:

$$C^*(T^*) = \frac{B^*(T^*)}{(T^*)^{1/4}}, \tag{4}$$

which is applicable in the range of the reduced temperatures between 20 and 100.

TABLE 1
Potential Parameters of Individual Combustion Products

Combustion product	Parameters used in Buckingham potential[16]			Parameters used in Lennard-Jones potential[12]	
	α	r_m (Å)	ε/k (K)	r_m (Å)	ε/k (K)
H_2O	13.5	3.35	38	2.889	180.0
H_2	13.5	3.34	37	2.868	29.2
O_2	15.0	3.73	132	3.575	117.5
CO_2	13.0	4.20	200	4.070	205.0
CO	13.0	4.05	120	3.763	100.2
NH_3	17.0	3.55	138	3.814	138.0
CH_4	13.5	4.29	154	3.817	148.2
NO	12.0	3.97	105	3.165	131.0
N_2	13.5	4.05	120	3.698	95.1
OH	13.5	4.21	80	4.21	80.0
H, N, O	13.5	3.50	80	3.50	80.0

r_m - separation distance corresponding to potential energy minimum

The calculation of the virial coefficients of a mixture of propellant gases is very complex task, which can be, with some approximations, solved on the basis of statistical mechanics.

In this paper the following equations are applied for the calculation of the second and third virial coefficient of the gaseous mixture[7]:

$$n^2B(T) = \left(\sum_i n_i\sqrt{B_i(T)}\right)^2 , \tag{5}$$

$$n^3C(T) = \left(\sum_i n_i\sqrt[3]{C_i(T)}\right)^3 , \tag{6}$$

where $B_i(T)$ and $C_i(T)$ are the second and third virial coefficients of individual species present in the mixture.

Calculation of Thermodynamic Functions of Combustion Products

The thermodynamic functions of combustion products as real gases are calculated by combining the thermodynamics laws and the virial equation of state:

- the molar internal energy of the gaseous mixture at T,V state[7]:

$$E(T, V) = E(T, V^0) - \frac{RT}{n}\left(\frac{n^2T}{V}\frac{\partial B(T)}{\partial T} + \frac{n^3T}{2V^2}\frac{\partial C(T)}{\partial T}\right) \tag{7}$$

where: $E(T, V^0) = \frac{1}{n}\sum_i n_i(E_T^0)_i = \frac{1}{n}\sum_i n_i\left[\left(H_T^0 - H_{298}^0\right)_i - RT + \left(H_{298}^0\right)_i\right]$

$$\frac{\partial B(T)}{\partial T} = \frac{1}{n^2}\left(\sum_i n_i\sqrt{B_i(T)}\right)\left(\sum_i \frac{n_i}{\sqrt{B_i(T)}}\frac{dB_i(T)}{dT}\right),$$ derived using Eq. (5)

$$\frac{\partial C(T)}{\partial T} = \frac{1}{n^3}\left(\sum_i n_i\sqrt[3]{C_i(T)}\right)^2\left(\sum_i \frac{n_i}{\sqrt[3]{C_i^2(T)}}\frac{dC_i(T)}{dT}\right),$$ derived using Eq. (6)

- the molar heat capacity of the gaseous mixture at a constant volume (C_V):

$$C_v = \frac{1}{n}\sum_i n_i(C_V^0)_i - \frac{R}{n}\left(\frac{2n^2T}{V}\frac{\partial B(T)}{\partial T} + \frac{n^3T}{V^2}\frac{\partial C(T)}{\partial T}\right) \tag{8}$$

- the molar heat capacity at a constant pressure (C_p):

$$C_p = C_v + R\left[\frac{\left(1 + \frac{nB(T)}{V} + \frac{n^2C(T)}{V^2} + \frac{n}{V}\frac{\partial B(T)}{\partial T} + \frac{n^2T}{2V^2}\frac{\partial C(T)}{\partial T}\right)^2}{1 + \frac{2nB(T)}{V} + \frac{3n^2C(T)}{V^2}}\right] \tag{9}$$

- the Helmholtz energy (A) of the gaseous mixture[7]:

$$A(T, V) = A(T, V^0) + \frac{RT}{n}\left(\frac{n^2B(T)}{V} + \frac{n^3C(T)}{2V^2}\right) \tag{10}$$

where: $A(T, V^0) = \frac{1}{n}\left\{\sum_i n_i\left[(G_T^0)_i + RT\ln\left(\frac{(n_i\ /\ n)p}{p_0}\right)\right] - nRT\right\}$,

$$(G_T^0)_i = \sum_i\left[(G_T^0 - H_{298}^0)_i + (H_{298}^0)_i\right]$$

- the chemical potential of individual gaseous species is calculated as partial molar Helmholtz energy[7]:

$$\mu_i = (G_T^0)_i + RT\ln\left(\frac{(n_i\ /\ n)p}{p_0}\right) + RT\left[\frac{\partial}{\partial n_i}\left(\frac{n^2B(T)}{V} + \frac{n^3C(T)}{2V^2}\right)\right]_{V,T,n_j} \tag{11}$$

The partial derivatives of the second and third virial coefficients in Eq. (11) are calculated by using Eqs. (5) and (6):

$$\frac{\partial\ [n^2B(T)\ ]_T}{\partial n_i} = 2\sqrt{B_i(T)}\left(\sum_i n_i\sqrt{B_i(T)}\right) = 2n\sqrt{B(T)B_i(T)} \tag{12}$$

$$\frac{\partial\ [n^3C(T)\ ]_T}{\partial n_i} = 3\ \sqrt[3]{C_i(T)}\left(\sum_i n_i\sqrt[3]{C_i(T)}\right)^2 = 3n^3\sqrt[3]{C(T)C_i(T)} \tag{13}$$

For solid combustion products no corrections of thermodynamic functions are applied, since they are considered as incompressible.

The values of thermodynamic functions in thir standard state are calculated from the enthalpy, which is in turn expressed as a function of temperature by the fourth degree polynomial.

RESULTS AND DISCUSSION

The obtained results have confirmed that the Gibbs energy minimization method is very suitable for the calculation of equilibrium composition of propellant combustion products. It is also shown that the modified Newton method, used to solve the system of equations mathematically describing the equilibrium state is of good convergence even in the case when assumed solutions considerably differ from the real ones.

However, the accuracy of the theoretical calculation of thermodynamic parameters of propellant gases, as well as the accuracy of interior ballistics calculation depends more considerably on the accuracy of the equation of state used to account for the real gases effects.

As already mentioned, the virial equation of state has a strong fundamental basis. However, when using this equation the problems appear in applying the accurate values of virial coefficients as functions of temperature, as well as in the calculation of the virial coefficients of the gaseous mixture. It may be stated that the situation in this field is such that a number of potentials can be used to calculate the values of the second virial coefficient, obtaining thus the results which are in reasonable agreement with the results of experiments, even at high temperatures. However, when the third virial coefficient is concerned, large differences exist.

For example, it can be seen from Figure 1 that the values of the second virial coefficients of water, obtained in different ways, are in reasonable agreement at higher temperatures (between 2500 and 5000 K the difference is less than 5 cm^3/mol). For carbon-dioxide the agreement is better at low temperatures, while at higher temperatures the difference between the lowest and the highest values approaches 15 cm^3/mol, i.e. almost 50%.

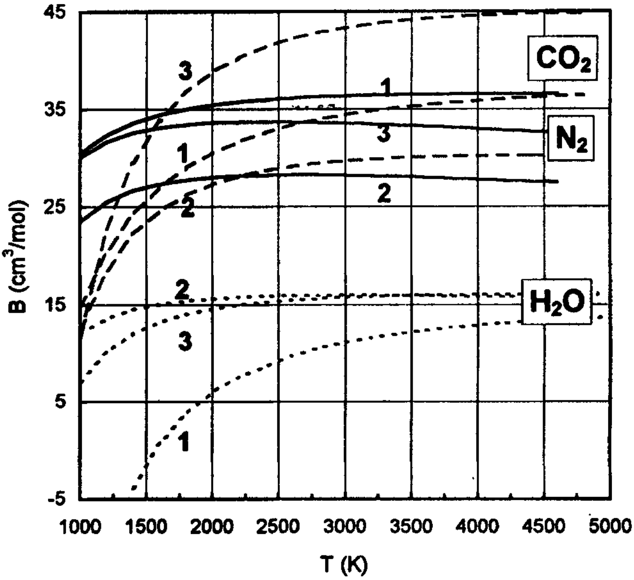

FIGURE 1

Second Virial Coefficient of H_2O, CO_2 and N_2 *vs*. Temperature
1) calculated by the equations given in Powell et al.; 2) calculated from the Buckingham potential; 3) calculated from the Lennard-Jones potential

As to other combustion products, it is founded out that there is an excellent agreement for hydrogen (Figure 2), while for nitrogen and carbon-monoxide the differences are in the range from 5 to 12 cm^3/mol, for temperatures between 2000 and 5000 K. Generally, the values of the second virial coefficient of individual species, calculated in different ways, differ up to 15 cm^3/mol, i.e. up to nearly 50%.

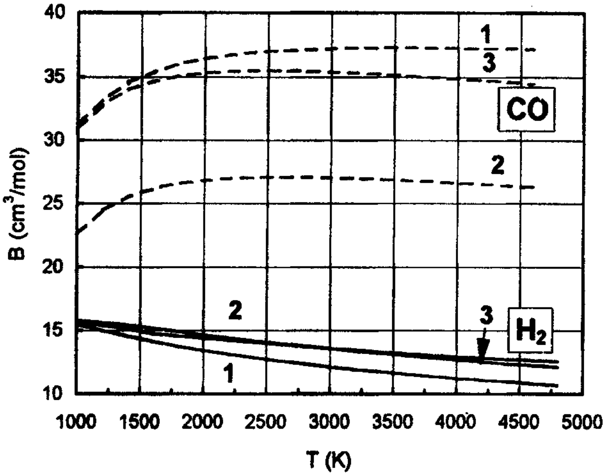

FIGURE 2
Second Virial Coefficient of H_2 and CO *vs.* Temperature
1) calculated by the equations given in Powell et al.; 2) calculated from the Buckingham potential; 3) calculated from the Lennard-Jones potential

The values of the third virial coefficients, calculated in different ways, differ more considerably (Figure 3 and 4). For example, the value of the third virial coefficient of water at 4500 K lies between 115 and 315 (cm^3/mol)^2, and for carbon-dioxide between 1100 and 1800 (cm^3/mol)^2, which means that the differences are greater than 50%. Similarly, the values of the third virial coefficient of CO, N_2 and H_2 differ 100-300 (cm^3/mol)^2.

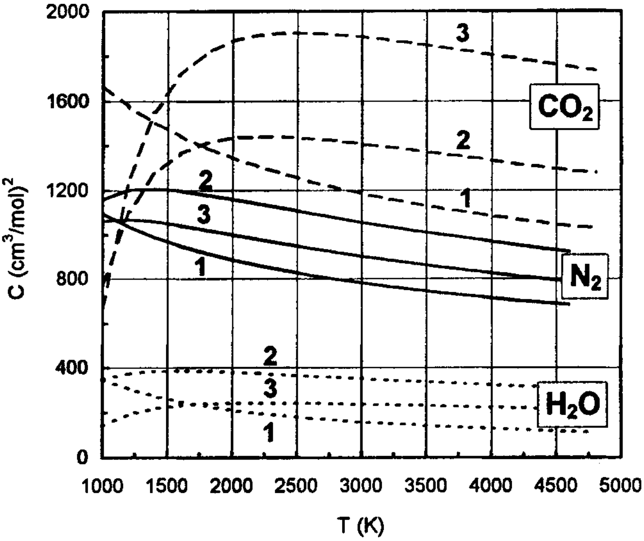

FIGURE 3
Third Virial Coefficient of H_2O, CO_2 and N_2 *vs.* Temperature
1) calculated by the equations given in Powell et al.; 2) calculated from the Buckingham potential; 3) calculated from the Lennard-Jones potential

It follows from the above considerations that the values of the virial coefficients of individual species, calculated from different potential equations, and by using equations derived from experimental measurements, are in considerable disagreement. The way it influences the calculation results, and the applicability of computer program BOMBA8 is illustrated on the example of three typical types of homogeneous propellants whose composition is given in Table 2.

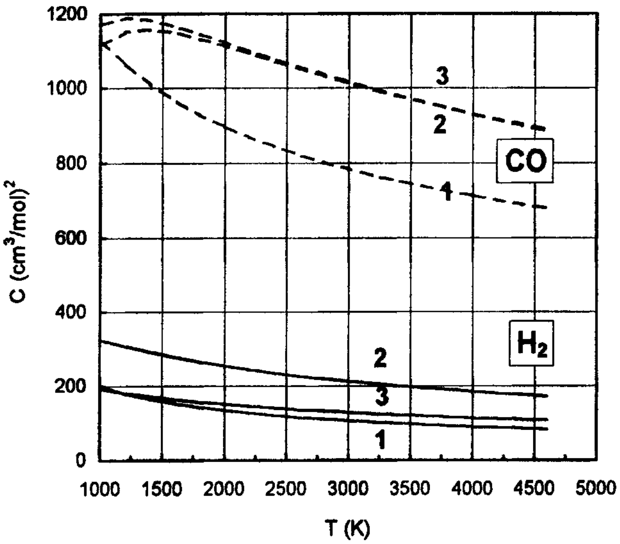

FIGURE 4
Third Virial Coefficient of H_2 and CO *vs*. Temperature
1) calculated by the equations given in Powell et al.; 2) calculated from the Buckingham potential; 3) calculated from the Lennard-Jones potential

The testing was performed by comparing the experimental values (with heat loss correction) and the calculated values of maximum pressure, specific energy, and covolume of propellants gases.

The experimental values of maximum pressure, taken from Ref. 19 and Ref. 22, were obtained using closed bomb having 700 cm^3 of the combustion chamber volume. As ignition charge 2 g of black powder was used[19,22]. The experimental values of the specific energy and covolume were calculated from the maximum pressure - loading density relationship, given by Noble-Abel equation[23].

The heat loss corrections are taken into account by applying

Miraur empirical equation (cited in Ref. 23) for the calculation of pressure corrections:

$$p_E = p_{EU} + C_M \frac{S_b p_{EU}}{V_b \Delta} \qquad (14)$$

where: p_E - maximum pressure with heat loss corrections
p_{EU} - maximum pressure without heat loss corrections (as measured)
C_M - empirical coefficient (dependent on propellant shape and size, i.e. duration of propellant combustion)
S_b - area of combustion chamber
V_b - volume of combustion chamber
Δ - loading density

The results of the comparison are given in Tables 3, 4, and 5.

TABLE 2
Chemical Composition of Propellants Used to Test the Computer Program

Propellant ingredient	PROPELLANT DENOTATION		
	BE0[19]	B00[22]	B30[22]
	Mass percent of ingredient (%)		
Nitrocellulose	97.66 (13.25% N)	57.04 (12.05% N)	36.38 (12.05% N)
Nitroglycerin	—	37.53	27.38
Nitroguanidine	—	—	30.46
Dibuthylphthalate	—	2.97	3.56
Diphenylamine	1.15	—	—
Graphite	0.14	—	—
Diethyleter	0.26	—	—
Ethyl centralite	—	2.26	2.06
Ethanol	0.16	—	—
Water	0.63	0.20	0.16

TABLE 3

Comparison of Measured and Calculated Values of Maximum Pressure

Propellant	Loading density (g/cm^3)	p_E (bar)	Calculated pressure (bar)			Ref.
			p_P	p_R	p_X	
BEO	0.150	1825	1875 (+2.74%)	1845 (+1.09%)	1894 (+3.78%)	19
	0.175	2184	2249 (+2.97%)	2213 (+1.33%)	2277 (+4.26%)	
	0.200	2571	2646 (+2.92%)	2602 (+1.21	2685 (+4.43	
B00	0.125	1544	1591 (+3.04%)	1569 (+1.62%)	1604 (+3.89%)	22
	0.150	1911	1966 (+2.87%)	1936 (+1.31%)	1986 (+3.92%)	
	0.175	2266	2361 (+4.19%)	2323 (+2.52%)	2390 (+5.47%)	
	0.200	2699	2777 (+2.89%)	2731 (+1.19%)	2817 (+4.37%)	
B30	0.125	1447	1512 (+4.49%)	1491 (+3.04%)	1520 (+5.04%)	22
	0.150	1821	1869 (+2.64%)	1843 (+1.21%)	1883 (+3.40%)	
	0.175	2182	2247 (+2.98%)	2215 (+1.51%)	2269 (+3.99%)	
	0.200	2573	2646 (+2.84%)	2608 (+1.36%)	2676 (+4.00%)	

Subscript denotation:

E -experimental values (with heat loss corrections)
P -virial coefficients calculated by the equations given in Powell et al.
R -virial coefficients calculated from the Buckingham potential
X -virial coefficients calculated from the Lennard-Jones potential

TABLE 4
Comparison of Measured and Calculated Values of Propellant Specific Energy

Propellant	Loading density (g/cm^3)	f_E * (kJ/g)	Calculated specific energy • (kJ/g)			Ref.
			f_P	f_R	f_X	
BEO	0.150 - 0.200	1.046	1.060 (+1.34%)	1.054 (+0.76%)	1.056 (+0.96%)	19
BOO	0.125 - 0.200	1.083	1.113 (+2.77%)	1.106 (+2.12%)	1.108 (+2.31%)	22
B30	0.125 - 0.200	1.009	1.048 (+3.68%)	1.042 (+3.27%)	1.043 (+3.37%)	22

* Mean values in the given range of loading densities

TABLE 5
Comparison of Measured and Calculated Values of Covolume of Propellant Gases

Propellant	Loading density (g/cm^3)	b_E * (cm^3/g)	Covolume (cm^3/g) *			Ref.
			b_P	b_R	b_X	
BEO	0.150 - 0.200	0.929	1.083 (+7.96%)	0.949 (+2.16%)	1.080 (+16.25%)	19
BOO	0.125- 0.200	0.976	1.003 (+2.77%)	0.949 (-2.77%)	1.080 (+10.66%)	22
B30	0.125- 0.200	1.083	1.052 (-2.86%)	1.011 (-6.65%)	1.122 (+3.60%)	22

* Mean values in the given range of loading densities

The correlation analysis of the experimental and calculated values of maximum pressure showed that the best agreement is obtained when the virial coefficients are calculated from the Buckingham potential, using the values of the intermolecular potential parameters given in Table 1, (p_R = 1.0149 p_E, r = 0.9996), while the worst agreement is obtained when the values of the reduced second virial coefficient obtained from the Lennard-Jones potential are used ($p_X = 1.0426\ p_E$, $r = 0.9995$). When the values of the second and third virial coefficients are calculated from the equations given in Powell et al., the following correlation is obtained: $p_P = 1.0308\ p_E$ ($r = 0.9996$).

It is evident that all calculated values of maximum pressure are consistently slightly greater than the experimental ones (maximum difference may reach about 5%). At the same time, the differences between the calculated values of maximum pressure are less than 3%. Taking into account the fact that the experimental values of maximum pressure are determined with an error of about ±3%[22], it follows that the agreement between the calculated and experimental values of maximum pressure is almost in the range of the experimental error.

A similar agreement is obtained between the calculated and experimental values of propellant specific energy (difference less than 4%), while slightly greater differences are obtained between the calculated and measured values of covolume (Table 5).

Considering the results presented in Tables 3, 4 and 5, it can be stated that there is a satisfactory agreement between the calculated and experimental values of pressure, specific energy, and covolume, in spite of the fact that the values of virial coefficients differ considerably. Such (unexpected) results may be explained by the fact that the corrections for nonideal behavior of propellant gases (i.e. influence of the second and third virial coefficients) are not too significant at a lower loading densities. For example, the corrections of pressure for the loading densities of 0.1 and 0.2 g/cm^3 are approximately 10% and 25%, respectively (Figure 5).

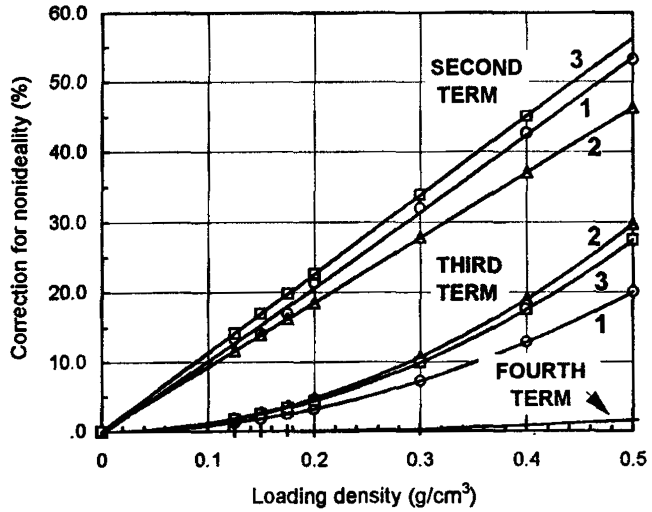

FIGURE 5
Influence of Second, Third, and Fourth Term in Virial Equation of State on Correction for Nonideal Behavior of Propellant Gases
1) calculated by equations given in Powell et al.; 2) calculated from Buckingham potential; 3) calculated from Lennard-Jones potential

The results above may be explained in the best way by the following example. At a loading density of 0.2 g/cm^3 the compressibility factor for the propellant denoted as B00 (Table 2) equals $Z=1+0.21+0.03=1.24$. It means that the second (nB/V) and third term (n^2C/V^2)in the virial equation of state are equal to 0.21 and 0.03 respectively. Since the molar volume of propellant gases for this loading density equals 123 cm^3/mol, it follows that the second and third virial coefficient of the mixture of propellant gases are 26 cm^3/mol and 455 $(cm^3/mol)^2$ respectively. Let us suppose that the value of the second virial coefficient is 50% greater (instead of 26 cm^3/mol it equals 39 cm^3/mol). The compressibility factor will be then $Z=1+0.32+0.03=1.35$, which means that the pressures calculated with the first and second value of the second virial coefficient will differ only for 8.8% [100(1.35-1.24)/1.24]. Similarly, if the value of the third virial coefficient is 50% greater, the resulting pressure will be only about 1.5% greater. For higher loading densities the corrections for nonideality becomes more considerable, as well as the influence of the second and third virial coefficients (Figure 5). This is the reason why the considerable disagreements in he values of the virial coefficients result in an acceptable agreement in the maximum pressure values, and propellant specific energy, particularly at low loading densities.

A rough calculation of the value of the fourth virial coefficient of the gaseous mixture (based on the procedure described by Xiong)[12], shows that the contribution of the forth virial coefficient to the maximum pressure becomes considerable (greater than 1%) if the loading density is greater than 0.4 g/cm^3. It means that in order to obtain a more accurate calculation for the loading densities above 0.4 g/cm^3, the fourth term in the virial equation of state should be used.

The computer program BOMBA8 is also tested by comparing the calculated values of maximum pressure for the double base propellant denoted as B00 (Table 2), with the results obtained by other computer programs for a similar gun propellant. For this comparison the virial coefficients are calculated using the equations given in Powell et al. The results of the comparison are shown in Figure 6.

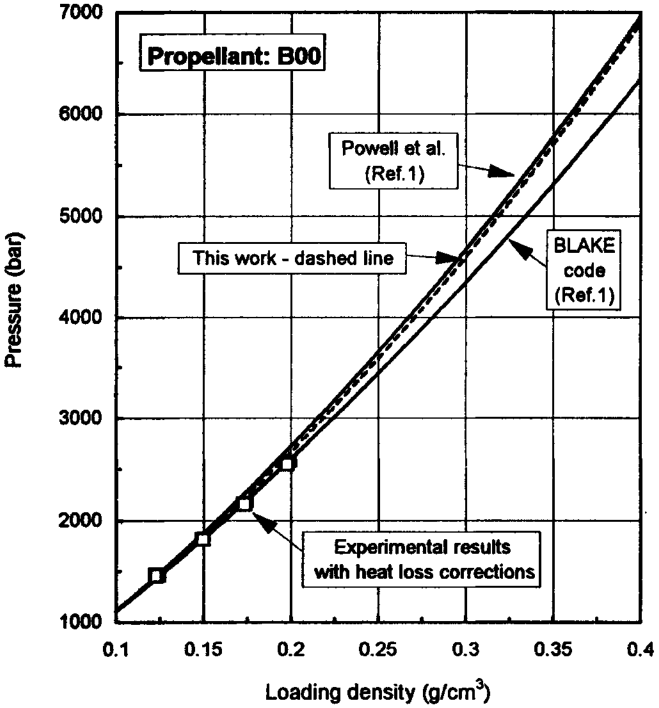

FIGURE 6
Pressure vs. Loading Density Calculated by Different Computer Programs

It can be seen from Figure 6 that a good agreement exists between the results obtained by BOMBA8 program and the results obtained by Powell et al. (authors have used the equation of state based on theoretical criteria which are also valid for the virial equation of state). The difference between the results obtained by the widely used computer code BLAKE (based also on the truncated virial equation of state), and BOMBA8 program is small at low loading densities, while it increases at higher loading densities (e.g. at 0.4 g/cm^3 it approximately equals 500 bar, or about 7.5%).

The comparison of calculated values of the heat capacity ratio, internal energy of propellant gases and combustion temperature showed that there is no considerable difference (Figure 7, 8, and 9) if the values of virial coefficients are calculated following the previously described three different ways.

The data from Figures 7 show that the difference in the values of the calculated propellant gases internal energy is not greater than 10 J/g (about 0.2%) if the loading density is in the range between 0.1 and 0.5 g/cm^3. This is consequence of the fact that the main part of the internal energy of propellant gases at these loading densities is due to heat (thermal energy - left part of Eq. 7), while only its small part is due to intermolecular interaction energy, i.e. consequence of nonideal behavior of gases (given by right part of Eq. 7).

For example, at loading density of 0.5 g/cm^3, the total internal energy equals 3946 J/g; the thermal part equals 3882 J/g (98.4%), while the part due to interaction energy equals only 64 J/g (1.6%). At 0.2 g/cm^3 the part of internal energy due to intermolecular interactions equals only about 0.5% of the total internal energy.

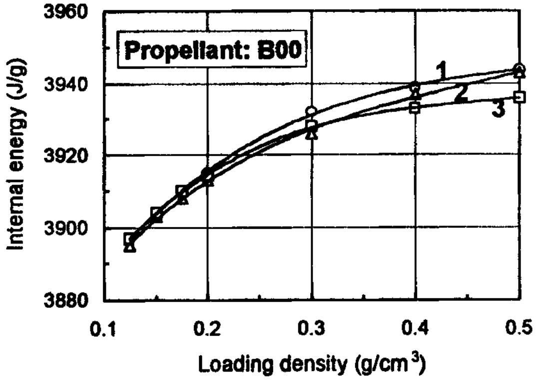

FIGURE 7
Internal Energy of Combustion Products *vs*. Loading Density for Propellant Denoted as B00
1) virial coefficients are calculated by equations given in Powell et al.; 2) virial coefficients are calculated from Buckingham potential; 3) virial coefficients are calculated from Lennard-Jones potential

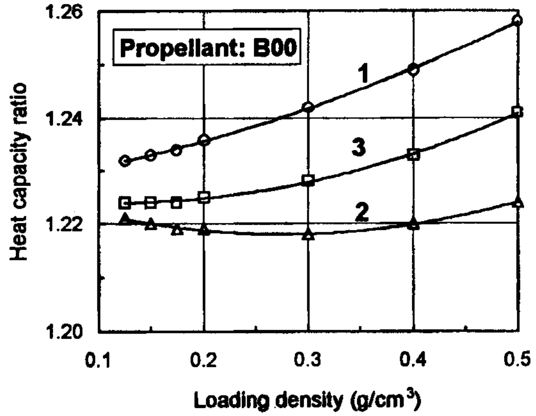

FIGURE 8
Heat Capacity Ratio *vs*. Loading Density for Propellant Denoted as B00
1) virial coefficients are calculated by equations given in Powell et al.; 2) virial coefficients are calculated from Buckingham potential; 3) virial coefficients are calculated from Lennard-Jones potential

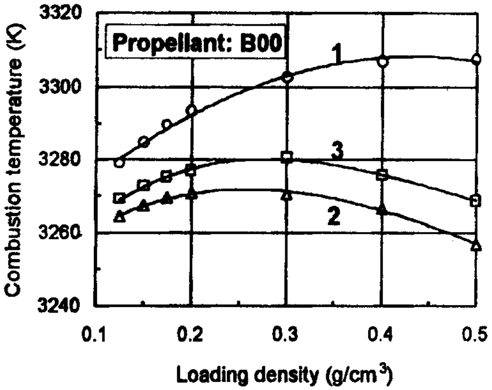

FIGURE 9
Combustion Temperature *vs.* Loading Density for Propellant Denoted as B00
1) virial coefficients are calculated by equations given in Powell et al.; 2) virial coefficients are calculated from Buckingham potential; 3) virial coefficients are calculated from Lennard-Jones potential

Generally, it can be stated that the corrections of thermodynamic functions of combustion gases (internal energy, Helmholtz energy, heat capacity ratio, etc.) for nonideal behavior, in the range of loading densities between 0.1 and 0.5 g/cm^3, are less than 3%. For comparison, the correction of pressure for nonidelity, for the same loading densities, reaches about 80%. Such small influence of corrections for nonidelity on the values of thermodynamic functions is the reason why the influence of different values of the virial coefficients on computed values of thermodynamic functions equals only a few percents.

CONCLUSIONS

Based on the presented results it can be stated that the described model of propellants combustion, and the computer program BOMBA8 can be used for the calculation of the thermodynamic properties of propellant gases with an error less than 5% (when the maximum pressure, specific energy and covolume are considered). At the same time it is shown that within the loading densities ranging between 0.1 g/cm^3 and 0.2 g/cm^3 the differences in the values of virial coefficients (i.e. calculation procedure - type of potential used and source of data) result in the differences between the values of maximum pressures and specific energies up to 3%.

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