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IMPROVING THE MODEL FOR DETERMINING THE COMPOSITION OF GUNPOWDER GASES DURING THERMAL DESTRUCTION OF GUNPOWDER IN A LIMITED VOLUME SPACE

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The object of this study is a model of the process of formation of products of thermal destruction of nitrocellulose powder at different values of pressure of the mixture of powder gases.

The work is aimed at eliminating the uncertainty in the list of powder combustion products. In many cases, the formation of condensed carbon during the shot is not taken into account, which does not correspond to the real process.

The process of formation of powder combustion products has been studied both under experimental conditions at a pressure of several MPa, and under shot conditions at a pressure of ~300 MPa and more. The proposed model makes it possible to explain the cause and conditions of condensed carbon formation. The possibility of formation of up to 10 % of condensed carbon from the initial mass of powder during the shot has been shown.

An improved model was built using the molar composition of the combustion products. The calculation of the specific volumes of gaseous reaction products with a change in the pressure of the gas mixture was carried out taking into account the change in their compressibility coefficient based on the Peng-Robinson equation. Within the limits of pressure values change during the shot process, the possibility of changing the equilibrium constant values in the range from ~40 % to twofold has been shown. The formation of condensed carbon is explained by the reaction of carbon monoxide disproportionation. The range of values of thermodynamic parameters of powder gases that ensure the possibility of this reaction was identified.

The proposed model could be used in the experimental determination of the composition and energy characteristics of a powder sample in the field based on the library method. Given the identified powder composition, the problem of internal ballistics could be solved for the prompt determination of shot parameters

Keywords: thermal destruction of powder, powder gases, compressibility coefficient, equilibrium model, condensed carbon

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1. Introduction

Since the discovery of nitrocellulose (NC) powder, related research, both theoretical and experimental, has been continuously conducted in various directions. All this time, models of varying complexity have been constructed that describe the processes of thermal destruction of powders. They were used to design new powder compositions and to solve the problem of internal ballistics. A common feature of these models is a significant discrepancy between the results of theoretical and laboratory studies and experimental data obtained during firing. Detailing (mathematical complication) of models and calculation methods does not lead to a fundamental reduction in discrepancies.

Thus, the authors of works [1–5] describe the composition of powder gases (PGs) differently not only in quantitative terms but also rely in their calculations on their different qualitative composition. As a result, the use of the results of theoretical studies in solving, for example, the problem of internal ballistics requires the use of empirical correction factors. Despite the long, detailed study of the process of thermal destruction of NC, one of the reasons for the discrepancies in the results of the studies may be the failure to take into account some factors that significantly affect the process of thermal destruction. Thus, in [1], the results of calculations show the possibility of the presence of up to 20 % condensed carbon in PG. At the same time, the results of their own experimental studies do not confirm this fact.

This situation is not critical when designing new weapons systems. Design solutions can be tested and adjusted by making prototypes and test firing. Due to intensive combat operations and the use of propellants of different, including beyond design, storage periods, a new task has emerged. There is a need to quickly assess the degree of degradation of the incoming propellants and its impact on firing parameters in the field, using minimal resources. At this stage, we,

researchers and practitioners, propose methods that could potentially solve this problem. They are based on the use of the results of a number of specially organized, simple experiments on the combustion of fixed propellant samples. For adequate interpretation of the data obtained, it is necessary to use a model of the thermal destruction process that has the minimum possible deviation of the predicted parameters of the powder gas formation process from the experimental data. Thus, the search for unaccounted factors that can manifest themselves in the process of thermal destruction and the development of an improved model taking them into account remains relevant.

2. Literature review and problem statement

Comparison of the thermal destruction data of NC propellants given in various sources and describing the results of both experimental and theoretical studies revealed a significant discrepancy.

In [1], it is noted that the composition of propellant gases may depend not only on the initial composition of the fuel mixture but also on its density in the combustion chamber and on the value of the pressure of the gas mixture. The conclusion is drawn on the basis of a comparison of the calculation results for three different models with experimental data. The calculation results also cover cases corresponding to values of gas mixture pressures of hundreds of MPa. At the same time, the calculation of the values of specific volumes of the mixture components is based on the ideal gas equations, which is not a valid approach for the declared pressure values. In [1], a contradiction is noted between the calculation results showing the possibility of free carbon content in PG of 20–30 % and the results of experimental studies, where it is absent. Possible reasons for such a contradiction are not analyzed.

In the empirical Kamlet-Jacobs model [2, 3] for the gross formula of the powder mixture $C_aH_bO_cN_d$, the composition of PG is assumed to be in the form of H_2O, H_2, CO_2, O_2, N_2, C_{crb} without the formation of CO (carbon monoxide) but with free carbon. The Le Chatelier-Millard model [4] in addition to the PG components of the previous model takes into account the possibility of CO formation. In [5] it is noted that in accordance with the Kistiakowsky-Wilson rule, PG should consist of gaseous products in the form of H_2O, CO, CO_2, H_2 and N_2. The lack of oxygen in the initial powder mixture is expressed in the formation of free hydrogen. In a number of works it is noted that such an assumption does not correspond to the composition of real PG. A common feature of works [2–5] is the empirical nature of the proposed models. Each of them satisfactorily approximates the composition of the thermal destruction products of NC powder only in a particular case of a combination of process parameters. The absence of a theoretical basis in modeling does not make it possible to use the calculation results obtained on their basis for forecasting.

In [6, 7] the presence of soot in the explosion products is indicated.

In [6], the presence of soot in the reaction products of thermal destruction of NC substances is stated. But only its morphological composition is considered in comparison with other non-explosive sources. The results of the work, as experimental, can serve to unconditionally state the formation of soot in such reactions. But it does not consider the mechanism of its formation.

In [7], the reaction of thermal destruction of three explosives of different compositions is considered. The reaction was carried out both in air and in an inert environment (argon environment). As in [6], the formation of soot is stated. A qualitative dependence of the amount of soot formed on the state of the reaction medium is noted: the values of temperature, pressure, the presence of oxygen in the air. Neither the nature of the reaction of soot formation nor its quantitative characteristics are considered. In [8], the presence of soot in the muzzle flash is considered an indisputable fact. The efforts of the authors are aimed at determining the distribution of temperature and volumetric content of soot in the muzzle flash based on the analysis of the intensity of the flash. The goal is to compile recommendations for reducing the visibility of the muzzle flash and flash. The work does not consider the possibility of the influence of the muzzle flash temperature on the presence of other combustible components in the muzzle flash, in addition to soot: carbon monoxide, hydrogen. The possibility of changing the PG composition depending on the composition of NC powder, loading density, changes in pressure and temperature during the PG expansion process is not taken into account.

In [9], the possibility of using the modified Kistiakovsky-Wilson rule to determine the PG composition is considered. Oxygen from nitro compounds is initially used for the complete oxidation of hydrogen atoms to form H_2O vapor. Then, carbon atoms are oxidized to CO. The remaining oxygen oxidizes CO to CO_2. But with such a scheme in the composition of gunpowder with a negative oxygen balance, oxygen is insufficient for the complete binding of carbon to CO. As a result, this can be the basis for explaining the presence of free carbon in the muzzle flash. But at the same time, the formation of H_2 and a significant amount of CO_2 is not explained. In practical studies, the real PG composition is not explained by either the basic or the modified Kistiakovsky-Wilson rule.

Quantitative differences in the research results can be explained by different levels of detail (mathematical complexity) of the models used. However, differences in the list of products of thermal destruction of gunpowder are also noted. In addition to chemical factors, as noted earlier, the composition of PG can be affected by the physical parameters of the process. In [7], the influence of the pressure on the amount of free carbon formed is noted. In this case, the influence of pressure at the stage of chemical transformation of the initial product of the powder mixture is considered. At the same time, two stages are distinguished in the firing process: pyrolytic (with chemical reactions) and thermodynamic. In [10], conditions are identified under which processes leading to the formation of free carbon can occur at the thermodynamic stage – the disproportionation reaction of carbon monoxide – the Boudouard-Bellrea reaction. The rate of this reaction can also depend on the pressure in the reaction medium. In the work, estimated calculations are performed showing the fundamental possibility of the occurrence of conditions for the disproportionation reaction. The equation of state of the gas is adjusted by using the covolume value. This approach is applicable to the estimated solution to the problem of internal ballistics but is not correct when determining the composition of PG. The covolume takes into account the real volume of gas molecules but does not take into account the effect of the pressure value on the change in the composition of the reaction products. Within the framework of, for example, the Van der Waals equation, the covolume corresponds only to coefficient *b*.

In [11], an equilibrium model was used to determine the composition of the thermal destruction products of NC powder, as in many studies. When constructing it, the constants of chemical equilibrium by mole fractions were used to take into account the composition of the mixture of gases and condensed carbon. This is rational at a constant pressure of the mixture of gaseous and condensed reaction products. In practice, in most cases, both in experimental studies and during a shot, the combustion of gunpowder occurs in a limited volume at a variable pressure, which complicates the use of such constants. The use in [11] of the equation of state of an ideal gas with correction using covolume, as in [10], does not allow one to take into account the influence of the pressure value on the change in the composition of the reaction products.

Our review of the literature [1–5] does not make it possible to identify a specific composition (list) of PG. This applies both to the case of determining their composition under laboratory conditions and to the composition of PG during a shot. The difference in determining the qualitative and quantitative composition of PG indicates the lack of consensus in the description of the mechanism of thermal destruction of NC powder. One explanation may be the discrepancy between the assumption of the frozen composition of PG under changing conditions during a shot. In addition, the conditions for conducting experiments are not the same. This can also affect the composition (list) of PG. And even more so, the conditions for conducting experimental studies do not correspond to the conditions of a real shot.

Our review [1–11] shows that even with the same composition of the powder charge, the composition of PG may be influenced by both additional, previously unaccounted for chemical reactions and thermodynamic parameters of the processes taking place. There is a need to correct the model, taking into account the possibility of the formation of PG of different compositions in experimental studies and under real firing conditions. Such a model might be in demand when using experimental data to calculate the parameters of a shot of an existing powder charge.

3. The aim and objectives of the study

The aim of our study is to construct an improved model for determining the composition of PG and their thermodynamic parameters as a result of thermal destruction of NC powder under experimental conditions and a real shot in a limited space. This will make it possible to use promptly obtained experimental data to determine the current state of the powder charge and the possibility of calculating the forecast of the parameters of the shot.

To achieve the goal, the following tasks were set:

– to determine possible causes and assess the degree of influence of various values of PG pressure on their composition in the processes of experimental research and shooting;

– to take into account the possibility of the formation of condensed carbon in the process of thermal destruction of nitrocellulose powder.

4. The study materials and methods

The object of our study is a model of the process of formation of thermal destruction products of NC powder. In works [6–8], the presence of soot in the reaction products is noted. Taking this into account, the model is improved taking into account the possibility of formation of condensed carbon.

The study is based on the assumption of formation of condensed carbon at the stage of expansion of PG during the shot after the end of powder combustion. A wide range of possible changes in the pressure value from units of MPa in experimental studies to hundreds of MPa during the shot served as the basis for taking into account the properties of real gas in the model.

The library method [12] is considered as a tool for determining the composition of NC powder. Unlike the original version of the method [12], the modeling of the powder combustion process is carried out for the conditions of a closed container of known volume. NC powders have a negative oxygen balance. The resulting PGs have a certain degree of flammability. In the case under consideration, preliminary filling of the container with air allows us to model the combustion process (afterburning) of the PG. Varying the weight of the burnt powder sample simulates the change in the ratio of fuel (powder gases) and oxidizer (air). Varying the quantitative composition of all chemical elements of the gross formula of the NC powder and the value of the enthalpy of formation allows us to simulate different compositions of powder, including degraded.

The process of combustion and expansion of powder occurs under high pressure: from ~50 MPa at the thermodynamic stage to ~300 MPa at the pyrodynamic stage. Such pressure values lead to high concentrations of PG components in limited volumes. In combination with high temperatures – from ~1000 K at the thermodynamic stage to ~3000 K at the pyrodynamic stage – it increases the rate of chemical reactions. Based on this, an equilibrium model of powder thermal destruction was used. The equilibrium model allows us to distribute the mass of chemical elements of the initial substance and the energy of its formation among a given list of reaction products and their temperatures. The list of reaction products must be specified.

The following qualitative composition of reaction products is considered in the calculations

$$H_2O,\ CO_2,\ CO,\ NO,\ H_2,\ O_2,\ N_2,\ U. \quad (1)$$

Here U is condensed carbon (soot).

The model is used both for the case of combustion in an experimental container (with a small value of pressure change) and will be used to solve the problem of internal ballistics [10] (high pressure). To determine the thermodynamic parameters, the equation of state of a real gas is used.

In the original representation of the library method [12], the combustion process in an open container at constant pressure was modeled for filling it [13]. The Dalton law equation was used as the closing equation – the pressure in the chamber is equal to the sum of the partial pressures of the reaction products. In the considered variant, the constant value is the volume of the closed container. Amagat's law (French *Emile Amagat*) is used as the closing equation – the total volume of the gas mixture is equal to the sum of the partial volumes V_i of the components at the temperature and pressure of the gas mixture. The partial volumes of the gaseous components of the PG mixture are determined from the ratio:

$$V_i = V_{im} \cdot n_i, \quad (2)$$

where V_{im} is the volume of one mole of the corresponding gaseous component of PG at the temperature and pressure of the gas mixture; n_i is the number of moles of the corresponding gaseous component of the PG mixture.

The value of $V_{i\,m}$ is calculated using the equation of state. The value of n_i is determined using the equilibrium model of thermal destruction of NC powder.

The model is constructed for thermal destruction of powder with a gross formula of the form:

$$C_{b_C}H_{b_H}O_{b_O}N_{b_N}, \quad (3)$$

although other chemical elements may be added if necessary. For the selected products of reaction (1), the equations of their formation are written as:

$$H_2O \rightleftarrows 2\cdot H+O;\ \ CO_2 \rightleftarrows C+2\cdot O;\ \ CO \rightleftarrows C+O;$$

$$NO \rightleftarrows N+O;\ \ H_2 \rightleftarrows 2\cdot H;\ \ O_2 \rightleftarrows 2\cdot O; \quad (4)$$

$$N_2 \rightleftarrows 2\cdot N;\qquad U \rightleftarrows C.$$

And the equations of chemical equilibrium for them are:

$$\frac{n_H^2\cdot n_O}{n_{H_2O}}=K_{n\,H_2O}\left(T,P\right),\ \ \frac{n_C\cdot n_O^2}{n_{CO_2}}=K_{n\,CO_2}\left(T,P\right),$$

$$\frac{n_C\cdot n_O}{n_{CO}}=K_{n\,CO}\left(T,P\right),\ \ \frac{n_N\cdot n_O}{n_{NO}}=K_{n\,NO}\left(T,P\right),$$

$$\frac{n_H^2}{n_{H_2}}=K_{n\,H_2}\left(T,P\right),\ \ \frac{n_O^2}{n_{O_2}}=K_{n\,O_2}\left(T,P\right), \quad (5)$$

$$\frac{n_N^2}{n_{N_2}}=K_{n\,N_2}\left(T,P\right),\ \ \frac{n_C}{n_U}=K_{n\,U}\left(T,P\right).$$

Equations of material balance:

– for [C]:

$$m\cdot\frac{b_C}{\mu_\Sigma}=n_{CO_2}+n_{CO}+n_C+n_U;$$

– for [H]:

$$m\cdot\frac{b_H}{\mu_\Sigma}=2\cdot n_{H_2O}+2\cdot n_{H_2}+n_H; \quad (6)$$

– for [O]:

$$2\cdot n_{air}\cdot\varepsilon_{O_2}+m\cdot\frac{b_O}{\mu_\Sigma}=n_{H_2O}+2\cdot n_{CO_2}+$$
$$+n_{CO}+n_{NO}+2\cdot n_{O_2}+n_O;$$

– for [N]:

$$2\cdot n_{air}\cdot\varepsilon_{N_2}+m\cdot\frac{b_N}{\mu_\Sigma}=n_{NO}+2\cdot n_{N_2}+n_N.$$

Here n_{air} is the number of moles of air in the container before the combustion of the powder; ε_{O_2}, ε_{N_2} is the proportion of the corresponding gas in the air; m is the mass of the powder subjected to thermal destruction; b_C, b_H, b_O, b_N are the number of atoms of the corresponding chemical elements in the gross formula of the powder; μ_Σ is the molecular mass according to the gross formula of the powder used.

The system of equations is closed by the Amag equation for the accepted list of gaseous products of thermal destruction of NC powder

$$V=n_{H_2O}V_{(m)\,H_2O}+n_{CO_2}V_{(m)\,CO_2}+n_{CO}V_{(m)\,CO}+n_{NO}V_{(m)\,NO}+$$
$$+n_{H_2}V_{(m)\,H_2}+n_{O_2}V_{(m)\,O_2}+n_{N_2}V_{(m)\,N_2}. \quad (7)$$

Here the terms of the right-hand side correspond to (2). In the material balance equation (6) for carbon there is a term n_U, taking into account the presence of condensed carbon. In equation (7) the corresponding term is absent. This is determined by the smallness of the volume of the condensed phase compared to the gas phase.

The reference literature provides constants of chemical equilibrium K_P, applied when using partial pressures of reaction products in calculations. Their values depend only on the temperature $K_P(T)$. The molar constants used in (5) depend on the temperature and pressure $K_n(T,P)$. They must be calculated using $K_P(T)$.

For the reaction equations (4), written in general form as

$$aA+bB \Leftrightarrow cC+dD, \quad (8)$$

the state of chemical equilibrium is written in the form of molar constants

$$\frac{n_C^c\cdot n_D^d}{n_A^a\cdot n_B^b}=K_n, \quad (9)$$

where a, b, c, d are the molar coefficients in (8); n_C, n_D, n_A, n_B are the number of moles of the corresponding substances A, B, C, D in (8); K_n is the chemical equilibrium constant for the number of moles.

The values of partial pressures p_i through molar fractions can be expressed as

$$p_i=X_i\cdot P_\Sigma=\frac{n_i}{\sum n_i}\cdot P_\Sigma, \quad (10)$$

where X_i are mole fractions; P_Σ is the total pressure of the gas mixture; n_i is the number of moles of the corresponding substance; Σn_i is the total number of moles of gaseous reaction products.

The chemical equilibrium constant through partial pressures for equation (8) takes the form

$$K_P=\frac{p_C^c\cdot p_D^d}{p_A^a\cdot p_B^b}. \quad (11)$$

Here the values of p_i are represented in bars. For this reason, P_Σ in (10) and in the subsequent transformations are represented in bars.

Taking into account (10), from (11) we obtain

$$K_P=\frac{\left(\frac{n_C}{\sum n_i}\cdot P_\Sigma\right)^c\cdot\left(\frac{n_D}{\sum n_i}\cdot P_\Sigma\right)^d}{\left(\frac{n_A}{\sum n_i}\cdot P_\Sigma\right)^a\cdot\left(\frac{n_B}{\sum n_i}\cdot P_\Sigma\right)^b}=$$
$$=\frac{n_C^c\cdot n_D^d}{n_A^a\cdot n_B^b}\cdot\frac{\left(\frac{P_\Sigma}{\sum n_i}\right)^c\cdot\left(\frac{P_\Sigma}{\sum n_i}\right)^d}{\left(\frac{P_\Sigma}{\sum n_i}\right)^a\cdot\left(\frac{P_\Sigma}{\sum n_i}\right)^b}=K_n\cdot\left(\frac{P_\Sigma}{\sum n_i}\right)^{c+d-a-b}, \quad (12)$$

hence

$$K_n\left(T,P\right)=K_P\left(T\right)\cdot\left(\frac{\sum n_i}{P_\Sigma}\right)^{c+d-a-b}, \quad (13)$$

which confirms the dependence of the value of K_n on the pressure of the gas mixture in addition to temperature. From (13), taking into account the equilibrium equation for the condensed phase (5), it follows

$$K_{nU}(T,P)=K_P(T)\cdot\left(\frac{\sum n_i}{P_\Sigma}\right)^{1-1}=K_P(T)\cdot 1=K_P(T). \quad (14)$$

Pressure affects the equilibrium position for reactions with a change in the number of moles of gas according to Le Chatelier's principle (French: *Henri Louis Le Chatelier*).

The values of V for the corresponding gas and P_Σ from (14) are related by the equation of state of a real gas.

The formation of free carbon during the shot is undeniable. This can be confirmed by the photograph in Fig. 1.

Fig. 1. An example of the presence of soot in the muzzle flash when firing (image from the storyboard of the authors' video)

The rationale for the mechanism of formation of condensed carbon is based on the assumption that conditions exist for the Boudouard-Bell reaction of disproportionation of carbon monoxide CO

$$2\cdot CO\uparrow \rightleftarrows U\downarrow +CO_2\uparrow +(Q). \quad (15)$$

Here, the symbol U denotes carbon in the condensed phase, for example in the form of soot.

In this reaction, a shift in equilibrium to the right becomes fundamentally possible with a decrease in the PG temperature, starting from the boundary at T~1200 K. At temperatures below T~700 K (400 °C), the equilibrium is almost completely shifted to the right, towards the formation of C – free carbon. But the rate of this reaction at low temperatures is low. Therefore, carbon monoxide is stable under normal conditions, although the reaction is exothermic. This is where its emergence (Anglicism from emergent) manifests itself.

This nature of the reaction is determined by its stages. At the first stage, gaseous carbon is formed

$$2\cdot CO\uparrow \rightleftarrows C_g\uparrow +CO_2\uparrow -(Q). \quad (16)$$

This stage is endothermic. It is the one that restrains the disproportionation of carbon monoxide under normal conditions. In the second stage, gaseous carbon condenses

$$C_g\rightarrow U+(Q). \quad (17)$$

This stage is exothermic, which leads to the overall exothermicity of reaction (15).

5. Construction of an improved model for determining the composition of powder gases

5. 1. Causes and extent of influence of the powder gas pressure on their composition

In an experimental study, when burning different amounts of gunpowder in a closed container, the pressure can be tens of bars. Under firing conditions, this value can reach several thousand bars. A change in the pressure leads to a change in the compressibility coefficient and, accordingly, to a change in the molar concentrations of gases even with their amount remaining unchanged. For the list of PGs (1) accepted for consideration, the compressibility coefficients Z were calculated for different temperatures and pressures based on the covolume, using the Van der Waals and Peng-Robinson equations. Fig. 2–4 graphically display the calculation results for some gases for different temperatures and pressures.

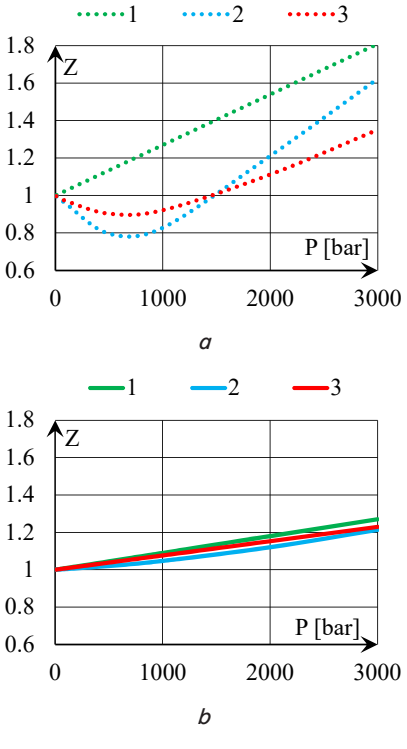

Fig. 2. Dependence of compressibility coefficient Z on the pressure value P for water vapor (H_2O): *a* – for a temperature of 1000 K; *b* – for a temperature of 3000 K: 1 – using the covolume value; 2 – using the van der Waals equation; 3 – using the Peng-Robinson equation

In addition to influencing the magnitude of molar concentrations, a change in the pressure value in accordance with (13) can affect the magnitude of the molar equilibrium constant even at a constant or slightly changing temperature of the gas mixture. Based on model (5) to (7), calculations were performed to simulate the process of thermal destruction of SB1 gunpowder [1] with the reduced gross formula $C_1H_{1.19}N_{0.384}O_{1.45}$ and the enthalpy of formation H_f= (– 96.38) [kJ/mol]. The formula is reduced to one car-

bon atom. Model calculations were performed for a vacuum container with a volume of 0.01 m^3 (10 liters) and two masses of gunpowder: 20 and 2400 grams, without taking into account the possibility of condensed carbon formation. The first option simulates conditions close to experimental ones. The second option corresponds to the firing conditions. The calculation results are given in Table 1.

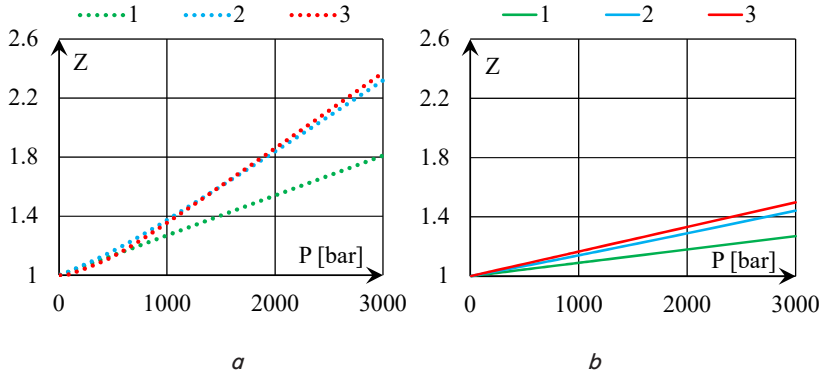

Fig. 3. Dependence of compressibility coefficient Z on the pressure value P for carbon monoxide (CO): a – for a temperature of 1000 K; b – for a temperature of 3000 K: 1 – using the covolume value; 2 – using the van der Waals equation; 3 – using the Peng-Robinson equation

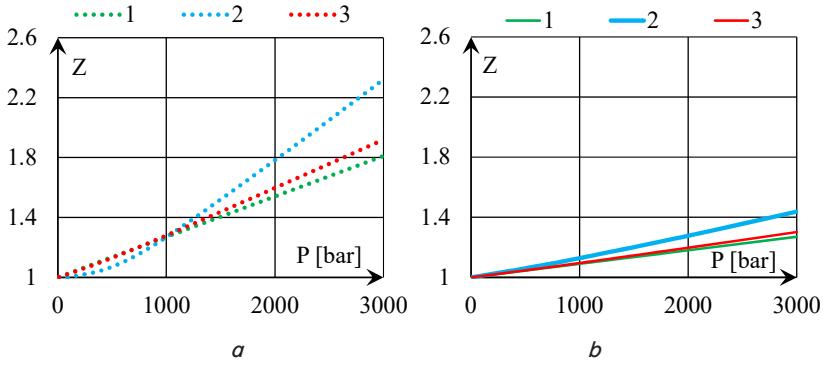

Fig. 4. Dependence of compressibility coefficient Z on the pressure value P for carbon dioxide (CO_2): a – for a temperature of 1000 K; b – for a temperature of 3000 K: 1 – using the covolume value; 2 – using the van der Waals equation; 3 – using the Peng-Robinson equation

Table 1

Molar equilibrium constants and molar fractions of thermal destruction products of NC powder

Component	m[gr]=20		m[gr]=2400		K_{20}/K_{2400}
	K_n	n_i/n_Σ	K_n	n_i/n_Σ	
CO_2	4.57E-29	1.19E-0.1	2.23E-29	9.24E-02	2.05
CO	3.42E-22	4.40E-01	2.38E-22	4.67E-01	1.43
H_2O	1.04E-14	1.35E-01	5.09E-15	1.59E-01	2.05
NO	6.69E-12	3.92E-10	4.67E-12	5.98E-08	1.43
H_2	3.63E-07	1.99E-01	2.53E-07	1.73E-01	1.43
O_2	6.71E-08	1.47E-13	4.69E-08	7.10E-11	1.43
N_2	3.13E-19	1.08E-01	2.18E-19	1.07E-01	1.43

Table 1 gives: m – mass of the burned gunpowder; K_n – molar equilibrium constant; n_i/n_Σ – fraction of the number of moles of the corresponding component in the total number of moles of the reaction products. The last column shows the ratio of the molar equilibrium constants for the experimental and firing conditions. For both masses of burned gunpowder, the same PG temperature T[K] = 2070 is achieved. When burning $m = 20$ g of gunpowder, the pressure in the container is $P = 14.7$ bar. When burning $m = 2400$ g – $P = 2530$ bar.

5. 2. Accounting for the possibility of condensed carbon formation during thermal destruction of nitrocellulose gunpowder

Using equations (5) to (7), calculations were performed to model the thermal destruction process of 2400 grams of SB1 gunpowder [1], taking into account the possibility of condensed carbon formation during cooling of PG. The results of calculations with and without taking into account the possibility of condensed carbon formation are shown in Fig. 5, 6. The results are represented in the form of plots of the number of moles of some gases included in the PG, depending on temperature.

The data slices of these calculations in the form of mass fractions of PG components from the mass of the powder are given in Table 2. Columns 2 and 3 (Table 2) show the mass fractions of the propellant gas components, respectively, without taking into account and taking into account the possibility of condensed carbon formation. These data correspond to the combustion temperature of the powder. Columns 4 and 5 (Table 2) show the data corresponding to the process of propellant gas expansion at the thermodynamic stage of the shot at a temperature of T=1000 K and 900 K, respectively. The possibility of condensed carbon formation is taken into account.

Using equations (5) to (7), calculations were performed to simulate the process of thermal destruction of SB1 gunpowder [1] in a 0.01 m^3 (10 liters) container filled with air. The mass of the gunpowder varied from 1 to 20 grams. Such calculations correspond to experimental studies on determining the composition of gunpowder using the library method [14]. The calculation results are shown in Fig. 7 as plots of changes in the number of moles of some PG components depending on the amount of gunpowder burned. It has a negative oxygen balance. The resulting PGs are not completely oxidized. Oxygen from the air in the container is used for their afterburning. When using gunpowder weighing up to 6 grams, there is more oxygen in the container than is necessary for complete afterburning of PG. In the calculations, part of the oxygen is taken into account as an oxidizer for complete afterburning of PG. Its remaining part and nitrogen are considered as ballast gases and are taken into account when determining the temperature of the entire gas mixture. When the powder mass is more than 6 grams, there is not enough oxygen for complete combustion of PG. But it is in this case that the conditions of variable values of the oxidizer and fuel necessary for filling the library are met [14]. The displayed boundary separates the areas with excess ($m < 6$ g) and deficiency ($m > 6$ g) of powder.

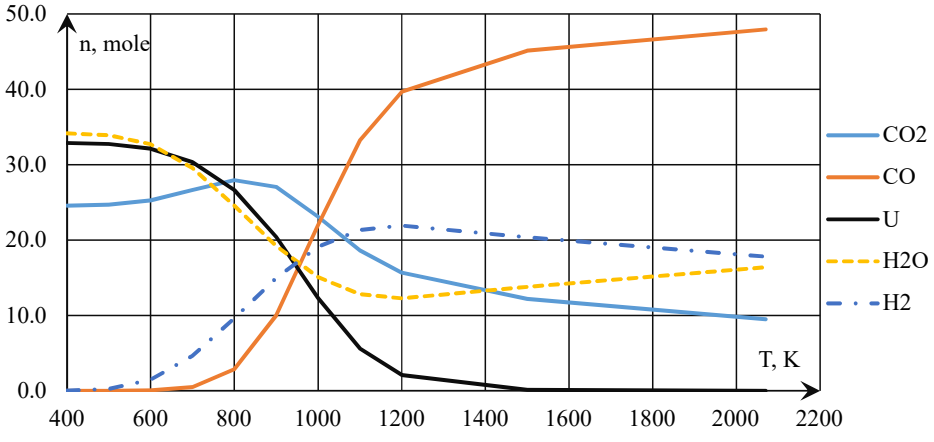

Fig. 5. The number of moles of gases and condensed carbon (*n*) from the composition of powder gases depending on temperature (*T*)

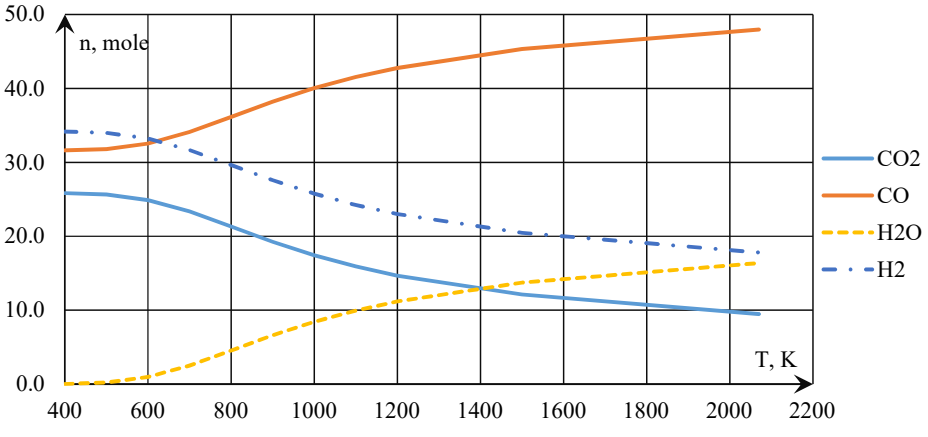

Fig. 6. The number of moles of gases (*n*) without taking into account the possibility of the formation of condensed carbon from the composition of powder gases depending on their temperature (*T*)

Table 2

Mass fractions of powder gases

Component	Proportion in % of powder weight (2400 g)			
	T[K]=2070	*T*[K]=2070	*T*[K]=1000	*T*[K]=900
	P[bar]=2530	*P*[bar]=2530	*P*[bar]=890	*P*[bar]=670
CO_2	17.4	17.4	42.3	49.6
CO	56.0	56.0	25.7	11.7
H_2O	12.3	12.3	11.3	14.4
NO	0.0	0.0	0.0	0.0
H_2	1.5	1.5	1.6	1.3
O_2	0.0	0.0	0.0	0.0
N_2	12.9	12.9	12.9	12.9
U	0.0	0.0	6.2	10.2

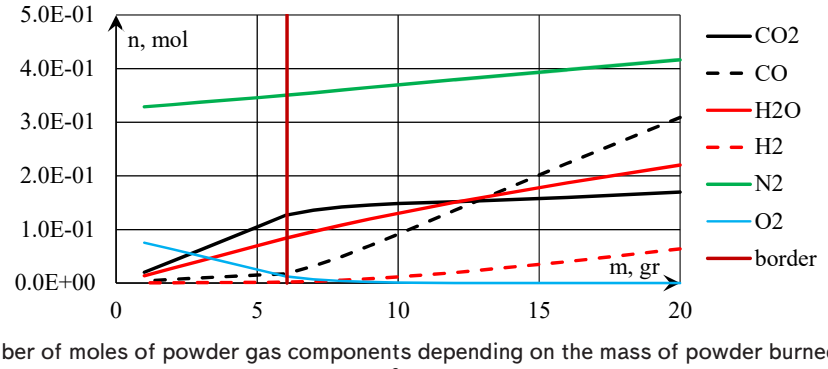

Fig. 7. The number of moles of powder gas components depending on the mass of powder burned in a container *V*=0.01 m^3 filled with air

Fig. 8 shows plots demonstrating the change in thermodynamic parameters of the PG mixture in the container.

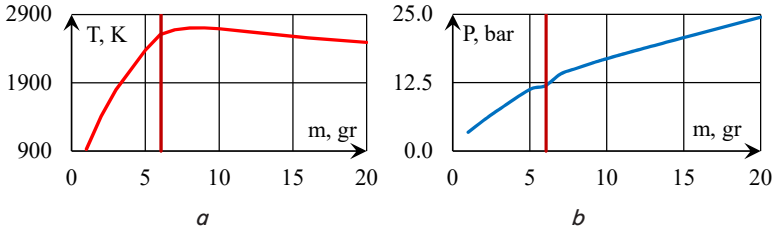

Fig. 8. Change in thermodynamic parameters of a mixture of powder gases depending on the mass of powder burned in a container V=0.01 m^3 filled with air: *a* – change in temperature; *b* – change in pressure

As in Fig. 7, the boundary separating the areas with excess and deficiency of oxygen (air) for afterburning of natural gas is shown.

6. Discussion of results based on constructing a model for the formation of powder gases

The gas compressibility coefficients calculated using different equations can differ significantly from each other, as indicated by the data shown in Fig. 2–4. This can be explained by the different nature of the change in the parameters taken into account when writing the equations and the calculated range of their change. The correspondence of these ranges in the equation of state and in the model determines the choice of the equation for calculating the compressibility coefficient. Equations (5) to (7) are designed for use at high temperatures (above the critical temperature for the gases under consideration) and in a wide range of pressure changes.

When using covolume, only the effect of the volume of molecules on the change in gas pressure is taken into account. The effect of temperature is taken into account within the framework of the equation of state of an ideal gas. In the Van der Waals equation, in addition to the volume of molecules, their interaction (attraction) is taken into account. The parameters of the equation are determined for moderate pressures and temperatures close to critical ones. Unlike taking into account the covolume or using the Van der Waals equation, the Peng-Robinson equation is constructed for high pressures (thousands of bars) and temperatures exceeding critical values. There are other equations of state, such as the Benedict-Webb-Rubin equation. It is the most accurate, but difficult to use and requires many parameters – eight volumetric constants for each substance. It is preferable to use for scientific purposes. The combination of the correspondence of the range of parameters for the application of the Peng-Robinson equation to the range of parameters for the application of our model and the simplicity of its application determines the reason for its use in studies on the formation of combustion products of NC powder.

It is proposed to use equations (5) to (7) in a wide range of changes in the gas mixture pressure. The conditions for filling the library correspond to small pressure values (tens of bars). Under these conditions, the methods used to obtain the data shown in Fig. 2–4 yield practically indistinguishable values of the compressibility coefficient Z=1, which corresponds to the equation of state of an ideal gas. But even under these conditions, the Peng-Robinson equation can be used as a single equation that allows us to use an improved model for the entire range of pressure changes.

The data given in Table 1 demonstrate the effect of pressure on the composition of powder gases even at the same temperature not only through the compressibility coefficient and, accordingly, through molar concentrations, but also through a change in accordance with (13) of the molar equilibrium constant. The change in the equilibrium constant values can be in the range from ~ 40 % to twofold. Thus, at the given pressure values, the quantitative share of carbon dioxide (CO_2) in the composition of the PG mixture may differ by ~ 22 %, water vapor (H_2O) by ~18 %, and hydrogen (H_2) by ~ 13 %. The influence of the pressure value may be one of the reasons for the differences in the PG compositions proposed by different authors for consideration (the Kamlet-Jacobs empirical model, the Le Chatelier-Millard model, the Kistiakowsky-Wilson rule, and the modified Kistiakowsky-Wilson rule). The related works do not specify the conditions for which the PG compositions are proposed for consideration. They could be different, which is one of the reasons for their differences. This feature could be highlighted by switching from calculating concentrations through partial pressures to molar concentrations. Taking into account the change in the values of equilibrium constants with changes in pressure values allows for the justified use of the results of experimental studies corresponding to small values of PG pressure for firing conditions.

The possibility of the formation of condensed carbon (soot) in the process of thermal destruction of NC powder is debatable only when considered theoretically. The photograph (Fig. 1) and data from [6–8] indicate the practical existence of such a process. In [8], the presence of soot in the muzzle blast is considered an indisputable fact. The authors' efforts are aimed at determining the temperature distribution and volumetric content of soot in the muzzle blast based on the analysis of flash intensity.

A feature of most calculations when solving the problem of internal ballistics is the determination of PG composition at the pyrodynamic stage of the shot, which corresponds to the high-temperature region.

The results of calculations taking into account the possibility of condensed carbon formation (Fig. 5) show that conditions for its formation do not arise at this stage. In addition, these results and calculations without taking into account the possibility of soot formation (Fig. 6) in the high-temperature region coincide. This is demonstrated numerically in columns 2 and 3 of Table 2. This may indicate the influence of the conditions of the process of expansion of powder gases on the formation of soot, and not the features of the model for calculating their parameters.

Consideration of processes at the thermodynamic stage of the expansion of the PG allows us to expand the range of phenomena taken into account. At this stage, high values of temperatures and pressures of PG are maintained, which does not exclude the possibility of chemical reactions. One of them may be the Boudouard-Bell reaction of disproportionation of carbon monoxide CO.

The magnitude of the pressure affects the shift of the equilibrium towards the formation of free carbon. In accordance with the Le Chatelier principle, an increase in the pressure of carbon monoxide shifts the equilibrium of reaction (15) to the right, towards a decrease in the value of the pressure of the gas mixture and the formation of free carbon. At the thermodynamic stage of the shot, conditions arise in the barrel that promote the accelerated course of reaction (15) with

a shift of the equilibrium to the right. In addition, the value of the PG temperature ~1000 K is in the range corresponding to the possibility of the occurrence of the disproportionation reaction (15). At the same time, the temperature is high so that the rate of the first endothermic stage of the reaction is noticeable. In addition, the value of the PG pressure at the end of the thermodynamic stage (30–90 MPa) promotes a fundamental increase in the reaction rate. The CO disproportionation reaction is second order. In this case, the rate of soot formation in the barrel system, compared to normal conditions (in many cases close to laboratory conditions in terms of pressure of ~0.1 MPa) at the same temperatures of the powder gases, increases from ~(30 MPa/0.1 MPa)^2 to (90 MPa/0.1 MPa)^2 times, or from ~90,000 to 800,000 times.

This can explain the contradictions similar to those that arose in [1] between the large calculated amount of free carbon in equilibrium processes and its absence in the experimental data. In [15], as in a number of other works, the influence of a change in the pressure value on the shift in equilibrium in reaction (15) is noted. A shift in equilibrium towards an increase in the yield of free carbon with increasing pressure is noted, but its mechanism is not explained. The value of the yield of free carbon can lead to the actualization of the use of the Bell-Boudoir reaction for the production of soot. In [16], the ability of the presence of hydrogen in a mixture with carbon monoxide to influence the increase in the amount of free carbon was noted. Water vapor [17] can have a similar effect on the growth of carbon nanotubes in the Bell-Boudoir reaction.

It is necessary to take into account the presence of both hydrogen and water vapor in the PG and their ability to influence the formation of free carbon in the carbon monoxide disproportionation reaction. Moreover, reaction (15) under certain conditions shifts to the right to such an extent (formation of free carbon) that it can be used for almost complete purification of the gas mixture from carbon monoxide [18].

The presented data indicate the need to use models that can take into account various factors that manifest themselves under different conditions of the implementation of the process of thermal destruction of the powder charge. In laboratory studies at low pressures, the formation of only gaseous products can be taken into account. At the same time, when studying the processes of a gunshot, it is necessary to take into account the possibility of the formation of a condensed phase in the form of free carbon. Taking these features into account, in both cases it is possible to use equilibrium models of PG formation. They can be considered as asymptotic models at low and high pressures.

The improved model, in contrast to [16, 17], makes it possible not only to note the effect of condensed carbon formation at a qualitative level but also to evaluate it quantitatively. Table 2 gives the results of calculations of PG composition for some temperatures, corresponding to the data in Fig. 5, 6. Comparison of the data in columns 2 and 3 (Table 2) indicates their coincidence for the process of gunpowder combustion both in the case of taking into account and not taking into account the possibility of condensed carbon formation. The data in columns 4 and 5 (Table 2) correspond to the thermodynamic stage of PG expansion. They demonstrate a change in the PG composition and the possibility of soot formation at this stage. Thus, at $T = 900$ K and $P = 670$ bar, the amount of condensed carbon can be up to 10 % of the initial mass of SB1 gunpowder [1]. In the case under consideration, this is ~ 240 g. From the data in Fig. 5 it also follows, for example, that at $T = 600$ K, the mass of condensed carbon can be up to 16.5 % of the gunpowder mass. This correlates with the calculated data [1] of 20 % of the gunpowder mass.

The improved model in the form of equations (5) to (7) allows for calculations of the quantity and parameters of thermal destruction products of NC powders for moderate pressure conditions – units or tens of bars. The calculated composition and parameters of the PG can then be used to fill in the library of their values [14]. Such a library allows for the composition of a sample of organic matter burned under experimental conditions [11].

The calculated data from the library [14] are used by comparing their values with the parameters obtained in the process of burning gaseous organic substances in a special device [19]. To obtain the required number of values, combustion is performed at different ratios of fuel and oxidizer. However, a number of problems arise when using the library method to determine the composition of NC powder:

– the powder mixture is in a condensed state. This was one of the reasons for the transition in the model from the standard use of partial pressures to the number of moles;

– thermal destruction of NC powder can occur without the use of other substances. In this case, the composition of the reaction products (powder gases) cannot be changed by simply changing the amount of gunpowder, the composition of which is determined, and is currently unchanged. To overcome this feature and to obtain the ability to influence the composition of the reaction products in accordance with the method proposed in [11], the container can be filled with various gases before the experiment. They can be oxidizers for the powder gases or contain an oxidizer. The use of, for example, oxygen or air allows the PG to be burned. In this case, a change in the amount of gunpowder also causes a change in the PG composition.

To confirm the possibility of calculating the composition of the propellant gases during their afterburning in air, calculations of the process parameters were performed for different powder masses – from 1 to 20 grams. The results obtained are shown in Fig. 7 as plots of changes in the number of moles of the propellant gases components depending on the amount of powder burned. The container was considered to be filled with air at atmospheric pressure. The calculation results are divided into two parts (marked “border”). The left part of the plot shows the results of complete afterburning of the powder gases. In this case, this corresponds to a powder mass of 1–6 grams. The right part of the plots shows the results of calculating the composition of the propellant gases with incomplete afterburning due to a lack of oxygen for this.

The boundary of division of the calculation results according to the principle of sufficiency of air for afterburning all powder gases determines part of the data suitable for determining the composition of the powder. An increase in the mass of powder in the left part of the plots leads to an increase in the total amount of propellant gases but practically does not change the ratio of their components. The composition of the propellant gases remains unchanged. For this reason, this part of the data cannot be used to determine the composition of the gunpowder using the library method [14]. In contrast, an increase in the mass of the gunpowder, corresponding to the right part of the plot, leads not only to an increase in the total amount of PG but also to a change in the ratio of their components, to a change in the composition of PG. In addition, with an increase in the pressure of PG mixture (Fig. 8, *b*), a decrease in its temperature occurs (Fig. 8, *a*). This part of the data is determined by a change in the ratio of components – the combustible part and the oxidizer. Together with a change in the temperature, it can serve as a basis for determining the composition of the gunpowder using the library method [14].

The nature of temperature change (Fig. 8, *a*) is determined by the ratio of the components. The left part of the plot shows the results of the increase in energy release with an increase in the mass of gunpowder during its complete afterburning in a container of constant volume. The right part of the plot shows the results of the decrease in the degree of afterburning of PG with a constant amount of air for an increasing amount of gunpowder. When burning from 6 to 9 grams of gunpowder, the PG temperature continues to increase slightly (from ~ 2600 K to ~ 2700 K). This can be explained by the outstripping increase in additional energy due to close to complete afterburning in relation to the increase in the amount of PG due to the increase in the mass of gunpowder. With a further increase in the mass of gunpowder and, accordingly, the mass of PG, the share of additional energy due to afterburning decreases. This is the reason for the decrease in the PG temperature (from ~ 2700 K at 9 grams of gunpowder to ~ 2490 K at 20 grams of gunpowder). As the powder mass increases and the degree of PG afterburning decreases, the limit of reduction can be the temperature value of ~ 2070 K (Table 2, columns 2, 3). It corresponds to the complete absence of PG afterburning, thermal destruction of the powder in a vacuum.

The equilibrium model for determining the composition of powder gases and condensed substances only distributes the amount of chemical substances in the powder between the products of its thermal destruction. The accuracy of the calculations correlates with the accuracy of determining their qualitative composition. In addition to gas components, condensed decomposition products of various mineral additives may be present in the products of thermal destruction. This requires determining the possible composition of the thermal destruction products at the preliminary (initial "production") stage.

The determined composition of the powder, although unknown, is constant in each specific case. When determining its composition using the library method, to ensure a variable composition of PG afterburning products, it is necessary to exceed the amount of combusted powder over a certain value ("border" in Fig. 7, 8). The excess value is determined by the composition of the preliminary gas filling of the container in which the PG afterburning occurs – for example, air or pure oxygen. On the one hand, the use of pure oxygen expands the possible range of variation of the values of the pressure of the afterburning products due to an increase in the possible amount of combusted powder. Accordingly, the number of pressure measurement points can be increased without reducing the accuracy. On the other hand, an increase in pressure leads to an increase in the probability of destruction of the test container structure. A compromise solution can be to use a mixture of air and oxygen.

7. Conclusions

1. Our studies have shown that the pressure value can influence the equilibrium composition of PG in a limited volume. It can manifest itself through the mechanism of changing the compressibility coefficient of gases and, accordingly, through changing their molar concentrations. The compressibility coefficient for different components of PG is different. Under firing conditions, it can be more than 2 times greater than the corresponding value for an ideal gas. In addition, a change in the molar equilibrium constants follows from a change in the pressure of the gas mixture. Their values for the experimental conditions and firing conditions can vary from ~40 % to twofold. This also leads to a change in the equilibrium composition of the gas mixture.

The effect of an increase in the amount of condensed carbon as one of the components in the products of thermal destruction of NC powder with an increase in the pressure noted in the literature can be explained, among other things, by the action of these mechanisms. The same applies to the explanation of disagreements in determining the composition of PG (the empirical Kamlet-Jacobs model, the Le Chatelier-Millard model, the Kistiakowsky-Wilson rule, the modified Kistiakowsky-Wilson rule).

2. As a result of our studies, the model that makes it possible to calculate the equilibrium composition of PG during thermal destruction of the NC propellant powder in a limited volume space has been improved.

The possibility of the carbon monoxide disproportionation reaction at a certain stage of the shot has been shown. This reaction can serve as a basis for explaining the formation of condensed carbon during the shot. The practical impossibility of such a reaction occurring at a low PG pressure (for example, under the experimental conditions) is indicated. This approach correlates with the literature data on the increase in the amount of soot with an increase in pressure during the combustion of propellant powder and explains this phenomenon.

The options for using the proposed approach have been considered both taking into account the possibility of condensed carbon formation and without taking this process into account. The coincidence of the results of calculating the PG composition using both options is demonstrated in the absence of conditions for the carbon monoxide disproportionation reaction. It is proposed to consider this improved model as asymptotic for the experimental conditions (low PG pressure) and shot conditions (high PG pressure). This approach makes it possible to use a single approach both when filling the library using the method [14] for determining the composition of the powder, and when solving the problem of internal ballistics based on the calculated composition of the powder.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study, as well as the results reported in this paper.

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Data availability

All data are available, either in numerical or graphical form, in the main text of the manuscript.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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