

Equation of State of Gas Detonation Products. Allowance for the Formation of the Condensed Phase of Carbon

E. R. Prueel^a and A. A. Vasil'ev^a

UDC 544.45

Published in *Fizika Goreniya i Vzryva*, Vol. 57, No. 5, pp. 74–85, September–October, 2021.
Original article submitted March 4, 2021; revision submitted March 4, 2021; accepted for publication April 21, 2021.

Abstract: A model of thermodynamics of a reacting mixture of rarefied gases and a suspension of condensed species is developed by using statistical physics methods. An NVT ensemble is considered for determining the detailed equilibrium chemical composition, and the minimum of the free energy of the mixture of possible species is found numerically. Tabular data for the species are used for determining the enthalpy and free energy of chemical compounds. An algorithm that allows the Chapman–Jouguet detonation parameters to be determined for a wide range of combustible mixtures is developed. The model is tested through comparisons of the predicted and experimental detonation velocities. Good agreement for mixtures with oxygen excess is demonstrated. For compositions with the formation of a significant amount of condensed carbon, the predicted and experimental detonation velocities agree reasonably well.

Keywords: carbon condensation in products, heterogeneous reaction products, equation of state of heterogeneous products, computer programs.

DOI: 10.1134/S0010508221050075

INTRODUCTION

Solving problems of fluid mechanics in explosions of combustible gases requires an equation of state that takes into account the formation of an equilibrium chemical composition of explosion products. As was noted in [1] and will be demonstrated in the present paper, the assumption about an equilibrium state inside the molecule and chemical equilibrium between the species provides an adequate quantitative description of a wide range of problems of combustion, shock waves, and detonation waves in gases.

The following hierarchy of models can be used to derive the equation of state for rarefied gases with weak interaction of molecules in the mixture under study:

(1) construction of thermodynamics of individual molecules with allowance for internal degrees of freedom;

(2) determination of the equilibrium chemical composition and construction of the equation of state of the mixture of reacting species;

(3) solution of gas-dynamic problems with allowance for the real equation of state.

Solving the first problem is a complicated laborious scientific problem of construction and calibration of the quantum-mechanical model of a molecule and creation of a thermodynamic database. Several centers developing independent thermodynamic “kernels” can be identified: multi-volume edition entitled “Thermodynamic properties of individual substances” edited by Glushko [1, 2] and its advanced version IVTANTHERMO [4, 5] in Russia, National Institute of Standards and Technology (NIST) [6] in the USA, and database of thermodynamic data and programs (FactSage) [7], which is a result collaboration of Canada and Germany.

An effective approach for determining the equilibrium chemical composition is the search for the extreme point of the corresponding thermodynamic potential, e.g., free energy. In this case, there arises a problem

^aLavrentyev Institute of Hydrodynamics, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia; prueel@hydro.nsc.ru; gasdet@hydro.nsc.ru.

of algorithm stability: the equilibrium concentrations of the mixture species under study may differ by many orders of magnitude, and it is not always possible to predict the basic composition. Nevertheless, in this way or another, this problem will be solved and a stable numerical algorithm that allows comparatively rapid determination of the equilibrium equation of state will be developed and implemented.

To apply the developed equation of state in solving gas-dynamic problems, it is necessary to combine the above-described parts effectively, with the computation speed, accuracy, and convenience of using the software system being retained. One of the examples of successful implementation is the NASA computer program [8, 9], which allows one to solve complex problems of combustion, shock waves, and detonation waves.

A specific complex problem is the allowance of the formation and extinction of condensed phases of, e.g., carbon, water, metals, and their oxides. In contrast to gases, the formation of the equilibrium chemical composition occurs more slowly, and the energy of fine particles being formed may differ from the data for the solid material. Nevertheless, correct allowance for the condense phase energy is an important scientific and technological problem.

The present paper describes constructing and testing of the model of the equation of state for reacting gases with possible formation of the condensed phase of carbon.

1. MODEL OF THERMODYNAMICS OF REACTING GASES

1.1. Thermodynamics of One Chemical Species

Let us consider the natural logarithm of the statistical sum $\ln(Z)$ for a gas consisting of noninteracting indiscernible molecules (ideal Boltzmann gas)

$$\ln(Z) = \ln \sum_n \exp \left(-\frac{E_n}{kT} \right),$$

where summation is performed over all energy states of the system E_n , k is the Boltzmann constant, and T is the temperature. Using the fact that the particles are indiscernible, we can replace the sum over all states for a system of N particles by the sum over the energy states of one molecule ε_k :

$$\ln(Z) = \ln \left\{ \frac{1}{N!} \left[\sum_k \exp \left(-\frac{\varepsilon_k}{kT} \right) \right]^N \right\}$$

or, for a large number N ,

$$\ln(Z) = N \ln \left[\frac{e}{N} \sum_k \exp \left(-\frac{\varepsilon_k}{kT} \right) \right].$$

The molecule energy can be written as

$$\varepsilon_k = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + \varepsilon'_k + \varepsilon^0,$$

where the first term is the energy of translational motion (p_x , p_y , and p_z are the momentum components, and m is the molecule mass), ε'_k are the energies of the internal degrees of freedom, and ε^0 is the energy of molecule formation from the basic chemical species at the zero temperature according to the Kelvin scale.

Partly replacing the sum by the integral over the phase volume, we obtain the expression

$$\ln(Z) = N \ln \left\{ \exp \left(-\frac{\varepsilon^0}{kT} \right) \exp \left[\frac{V}{N} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \right] \times \sum_k \exp \left(-\frac{\varepsilon'_k}{kT} \right) \right\},$$

where V is the system volume, and \hbar is the Planck constant. We introduce the pressure $p_0 = 101\,325$ Pa corresponding to the conditions of the standard state of gases according to [2] and rewrite the expression via the pressure p :

$$\ln(Z) = N \left\{ -\frac{\varepsilon^0}{kT} + 1 + \ln \left[\frac{kT}{p_0} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \right] \times \sum_k \exp \left(-\frac{\varepsilon'_k}{kT} \right) \right\} + \ln \left(\frac{p_0}{p} \right).$$

Using the approach [2], we replace the term in the middle by a tabular function depending only on temperature $f(T)$:

$$\ln(Z) = N \left[-\frac{\varepsilon^0}{kT} + 1 + f(T) + \ln \left(\frac{p_0}{p} \right) \right],$$

or, in the variables (T, V, N) ,

$$\ln(Z) = N \left[-\frac{\varepsilon^0}{kT} + 1 + f(T) + \ln \left(\frac{p_0 V}{N k T} \right) \right]. \quad (1)$$

The formula for the statistical sum (1) is a key expression. All other thermodynamic parameters of the chemical species are expressed via this formula.

Let us now express the free energy F , internal energy E , and enthalpy H via $\ln(Z)$ [10]:

$$F(T, V, N) = -kT \ln(Z),$$

$$E(T, V, N) = kT^2 \left(\frac{\partial \ln(Z)}{\partial T} \right)_V,$$

$$H(T, V, N) = kT \left[\left(\frac{\partial \ln(Z)}{\partial \ln(V)} \right)_T + \left(\frac{\partial \ln(Z)}{\partial \ln(T)} \right)_V \right],$$

or, via the tabular function $f(T)$:

$$F(T, V, \nu) = \nu \left[e_0 - RT \left(1 + f(T) + \ln \left(\frac{p_0 V}{\nu RT} \right) \right) \right],$$

$$e(T) = e_0 + RT^2 \frac{\partial f(T)}{\partial T} - RT,$$

$$h(T, p) = e_0 + RT^2 \frac{\partial f(T)}{\partial T}$$

(e and h are the internal energy and enthalpy per one mole of the substance, and e_0 is the energy of formation of one mole of molecules at the zero temperature according to the Kelvin scale) for gases and

$$F(T, V, \nu) = \nu [e_0 - RT(1 + f(T))],$$

$$e(T) = e_0 + RT^2 \frac{\partial f(T)}{\partial T} - \frac{p_0 \mu}{\rho_0},$$

$$h(T, p) = e_0 + RT^2 \frac{\partial f(T)}{\partial T} + \frac{(p - p_0) \mu}{\rho_0}$$

(μ is the molar mass of the species, and ρ_0 is its unchanged density) for condensed species.

As an example, Figs. 1–3 show the internal energy E and heat capacity c_v/R for some species.

A helium atom is a good example of a system without internal degrees of freedom; its heat capacity in a wide range of temperatures is completely determined by three translational degrees of freedom and has the value $3/2R$ (Fig. 1).

A nitrogen molecule N_2 has many internal degrees of freedom, and the dependence of its heat capacity on temperature is much more complicated: at $T \leq 500$ K, the main contributions are made by three translational and two rotational degrees of freedom ($c_v = 5/2R$); at high temperatures, vibrations become unfrozen ($c_v = 7/2R$); finally, at $T > 10\,000$ K, there arise excited electron states (Fig. 2).

Using the tabular dependence of the internal energy on temperature, one can describe the complex dependence of the heat capacity on temperature and the phase transition of melting for graphite (Fig. 3).

The following references were used for determining the thermodynamic characteristics of individual species: for basic, comparatively simple molecules, we used the multi-volume reference book edited by Glushko [2] supplemented with volumes V and VI [3], including its electronic version [4, 5]; for long hydrocarbons, we used the data from [11]. The National Institute of Standards and Technology (NIST) in the USA [6] is a place where thermodynamic data are actively accumulated nowadays.

Despite different standards of thermodynamic data representation, we managed to use the results from various references in our computations. The implemented

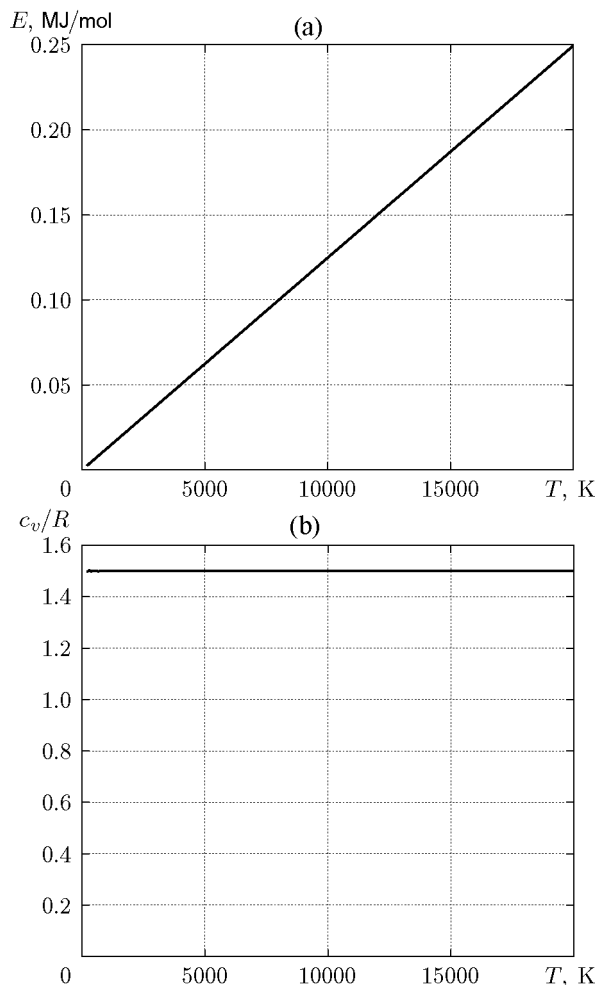


Fig. 1. Internal energy (a) and heat capacity (b) versus temperature for one mole of helium atoms.

algorithm allows one to use a single approach for quantification of the thermodynamic characteristics of both gaseous and condensed species.

1.2. Thermodynamics of a Mixture with a Frozen Chemical Composition

Let us consider a mixture with a known chemical composition consisting of ν_i moles of mixed gaseous species and a mixture of condensed species. Let us determine the necessary parameters, assuming the equilibrium states in terms of temperature and pressure between the species. The mass of the mixture is $M = \sum_i \nu_i \mu_i$, where summation is performed over all species. The total density is $\rho = M/V$. The volume occupied by the gaseous species is $V_g = V - \sum_i \nu_i \mu_i / \rho_0$, where summation is performed over the condensed species. The total pressure of all gaseous species is $p = \sum_i \nu_i RT / V_g$, where summation is performed over all gaseous species.

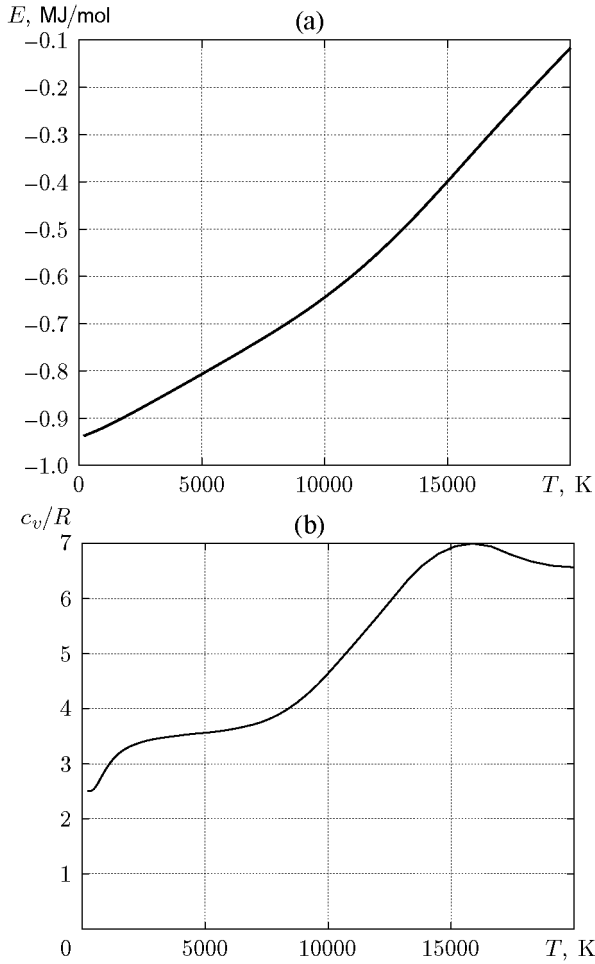


Fig. 2. Internal energy (a) and heat capacity (b) versus temperature for one mole of nitrogen molecules.

We used the above-presented relations to express the total free energy and the internal energy and enthalpy normalized to mass:

$$F(T, V, \nu_1 \dots \nu_k) = \sum_i F_i(T, V_g, \nu_i),$$

$$E(T, \nu_1 \dots \nu_k) = \sum_i \nu_i e_i(T)/M,$$

$$H(T, p, \nu_1 \dots \nu_k) = \sum_i \nu_i h_i(T, p)/M.$$

As the basic parameters for setting the state of the mixture, we choose the chemical composition, density, and temperature. The algorithm allows numerical determination of pressure, internal energy per unit mass, and partial derivatives of the basic parameters:

$$E(T, \rho, \nu_1 \dots \nu_k), p(T, \rho, \nu_1 \dots \nu_k), \quad (2)$$

$$\left(\frac{\partial E}{\partial T}\right)_\rho, \left(\frac{\partial E}{\partial \rho}\right)_T, \left(\frac{\partial p}{\partial T}\right)_\rho, \left(\frac{\partial p}{\partial \rho}\right)_T. \quad (3)$$

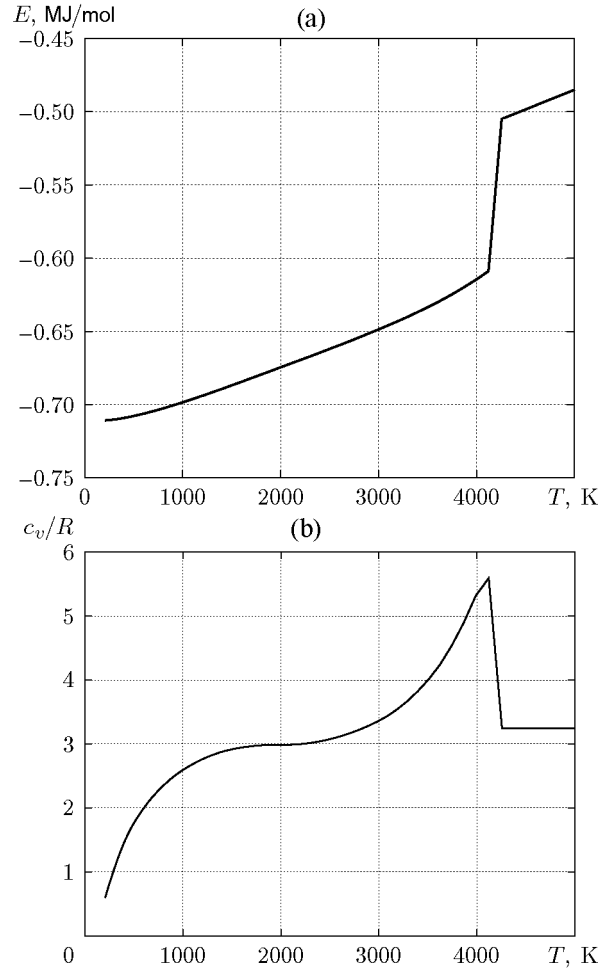


Fig. 3. Internal energy (a) and heat capacity (b) versus temperature for one mole of graphite.

All other thermodynamic parameters are calculated by the formulas

$$c_v = \left(\frac{\partial E}{\partial T}\right)_\rho, \quad (4)$$

$$c_p = \left(\frac{\partial E}{\partial T}\right)_\rho + \left[\frac{p}{\rho^2} - \left(\frac{\partial E}{\partial \rho}\right)_T\right] \left(\frac{\partial p}{\partial T}\right)_\rho / \left(\frac{\partial p}{\partial \rho}\right)_T, \quad (5)$$

$$c_{\text{sound}} = \left(\frac{\partial p}{\partial \rho}\right)_S^{1/2} = \left[\left(\frac{\partial p}{\partial \rho}\right)_T \frac{c_p}{c_v}\right]^{1/2}, \quad (6)$$

$$\gamma = \left(\frac{\partial p}{\partial \rho}\right)_S \frac{\rho}{p} = \left(\frac{\partial p}{\partial \rho}\right)_T \frac{c_p \rho}{c_v p}, \quad (7)$$

where c_v and c_p are the heat capacities per unit mass at constant volume and pressure, respectively, c_{sound} is the velocity of sound, and γ is the ratio of specific heats.

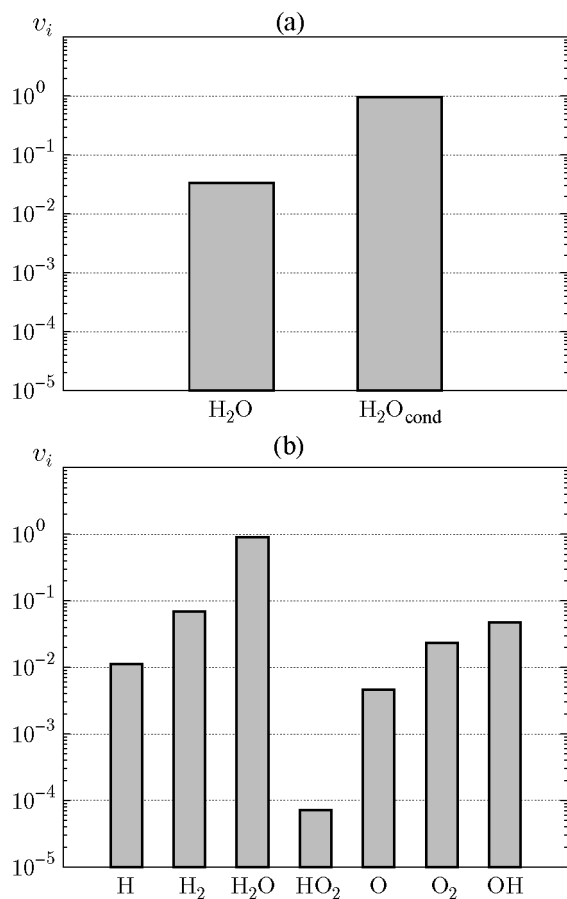


Fig. 4. Example of the calculation of the equilibrium chemical composition of the $2H + O$ mixture (water) at temperatures of 300 (a) and 3000 K (b) (the density is 1.0 kg/m^3).

1.3. Thermodynamics of a Reacting Mixture

To describe the algorithm of searching for the equilibrium chemical composition, we consider a system with the following possible reactions: one forward reaction of dissociation of the nitrogen molecule N_2 into two nitrogen atoms N ($N_2 \rightarrow 2N$) and one backward reaction of synthesis of the N_2 molecule from two N atoms ($2N \rightarrow N_2$).

At a fixed temperature, volume, and total number of moles of nitrogen atoms ν_0 , the thermodynamic equilibrium state corresponding to the minimum of the free energy of the mixture:

$$\begin{aligned} & F(T, V, \nu_{N_2}, \nu_N) \\ &= F_{N_2}(T, V, \nu_{N_2}) + F_N(T, V, \nu_N) = \min, \\ & \nu_N + 2\nu_{N_2} = \nu_0. \end{aligned}$$

For searching for the minimum of the potential, we used a numerical algorithm of iterative improvement of

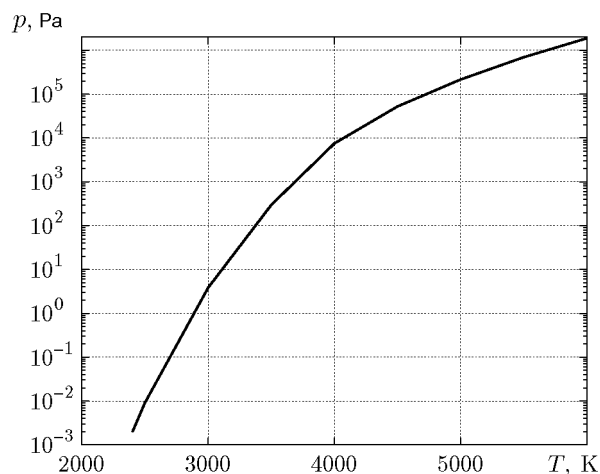


Fig. 5. Pressure of saturated vapors of carbon versus temperature.

the chemical composition. From the balance condition of the number of species, we chose the initial chemical composition (number of moles ν_{N_2} and ν_N): this composition was either arbitrary or chosen on the basis of a good initial approximation from previous computations. Based on the chosen composition, we calculated the current value of F_0 . The composition was varied along the forward reaction $\nu'_{N_2} = \nu_{N_2} - \delta$, $\nu'_N = \nu_N + 2\delta$, where δ is the reduction of the number of moles N_2 . A test value $F' = F(N'_{N_2}, N'_N)$ was calculated for the changed composition; if this value was smaller than the current value, the test composition was accepted as the current composition, and the composition was again varied along the forward reaction. In the opposite case, the composition was varied along the backward reaction: $\nu'_{N_2} = \nu_{N_2} + \delta$ and $\nu'_N = \nu_N - 2\delta$. A test value $F' = F(\nu'_{N_2}, \nu'_N)$ was calculated for the changed composition; if it was smaller than the current value, the test composition was accepted as the current composition, and the composition was again varied along the backward reaction. If neither the forward reaction nor the backward reaction reduced the potential value, the step δ was reduced, and the procedure was repeated.

Thus, an approximate solution was available at any stage of the algorithm, and this solution was then improved to desired accuracy. The characteristic normalized accuracy of composition calculation was 10^{-6} . This is fairly sufficient for stable operation of the entire algorithm of computing the thermodynamic parameters and for determining the gas-dynamic characteristics of the modeled flow.

The above-described algorithm ensures stable operation with gaseous and condensed phases in a wide range of temperatures and allows the formation and

deletion of condensed species in a unified manner. Figure 4 shows the equilibrium chemical compositions of the $2\text{H} + \text{O}$ mixture (water) at temperatures of 300 and 3000 K.

Using a similar algorithm, we considered the “reaction” of the formation of equilibrium phases of vapors and condensed species. For example, the mixture contains condensed carbon C_{cond} and gaseous carbon C_{gas} . They can exchange atoms, which can be presented as the reaction $1C_{\text{cond}} \leftrightarrow 1C_{\text{gas}}$. Minimizing the free energy of the mixture, we can find the equilibrium relationship between the phases (Fig. 5).

For determining the necessary thermodynamic parameters, we used Eqs. (2)–(7), but the chemical composition was assumed to be equilibrium.

Two models with allowance for the condensed phase of carbon were tested in the computations: C_c (formation of the equilibrium condensed phase of carbon is possible) and C_g (formation of condensed carbon is forbidden). It is seen from Fig. 5 that the pressure of saturated vapors is small in the entire range of temperatures typical for detonation of combustible gases. Carbon vapors are thermodynamically non-beneficial; as is shown below, the ban of condensed phase formation does not lead to a significant increase in the gaseous carbon fraction. The excess of gaseous carbon becomes aggregated with hydrogen, forming simple hydrocarbons (CH_4 and C_2H_2).

In Fig. 5 and further on, the gaseous carbon concentration is assumed to be the total concentration of carbon polymers: C, C_2 , C_3 , C_4 , and C_5 .

2. DETONATION FLOW PARAMETERS

2.1. Construction of the Shock Adiabats

For shock adiabat construction, the following nonlinear Hugoniot equation was solved numerically:

$$E_2 - E_1 - \frac{p_2 + p_1}{2} \left(\frac{1}{\rho_1} - \frac{1}{\rho_2} \right) = 0.$$

For specified initial parameters of the mixture (E_1 , p_1 , and ρ_1), the wave intensity was fixed by setting the temperature T_2 . Only one unknown parameter was left in the Hugoniot equation (ρ_2), which was found numerically [12].

Examples of the shock adiabats for the frozen (p_{fr}) and equilibrium (p_{eq}) compositions of the $2\text{H}_2 + \text{O}_2$ mixture in the pressure–specific volume coordinates are presented in Fig. 6a.

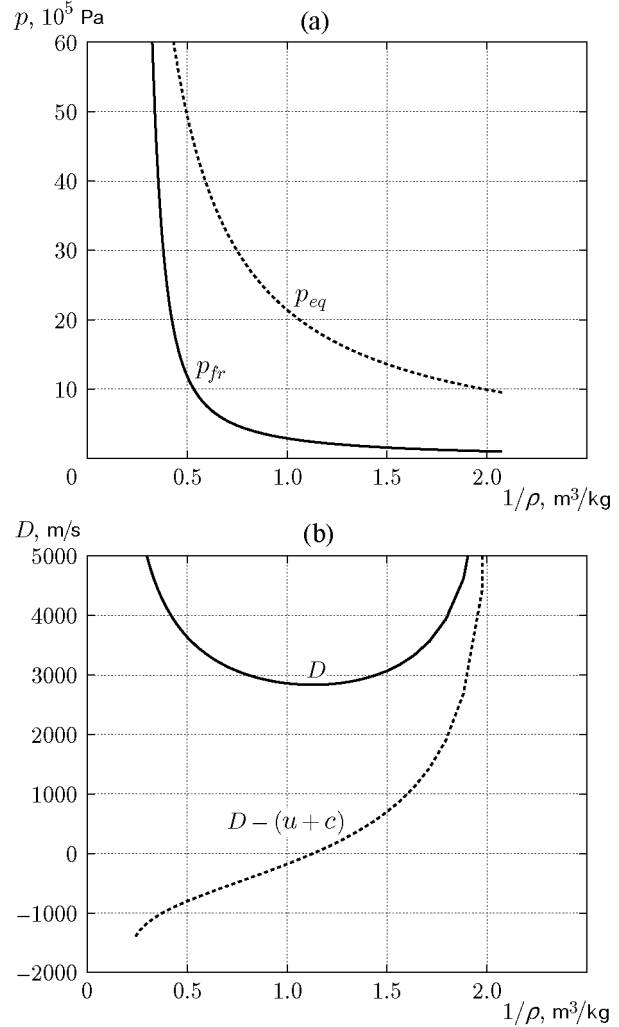


Fig. 6. Example of the computations of the frozen and reacting shock adiabats of the $2\text{H}_2 + \text{O}_2$ mixture under the initial conditions $T_0 = 300$ K and $p_0 = 10^5$ Pa. Pressure (a) and velocity (b) as functions of the specific volume.

2.2. Construction of the Detonation Adiabats

For determining the Chapman–Jouguet detonation parameters, we constructed the shock adiabat for the reacting mixture of combustible gases and found a point with the condition $D = u + c$, where D is the wave front velocity, u is the mass velocity of the substance behind the front, and c is the equilibrium velocity of sound.

An example of the corresponding adiabats for the $2\text{H}_2 + \text{O}_2$ mixture in the front velocity–specific volume coordinates is shown in Fig. 6b. It is seen that an arbitrary criterion can be used for determining the Chapman–Jouguet point on the shock adiabat: the point of touching of the Michelson straight line and the

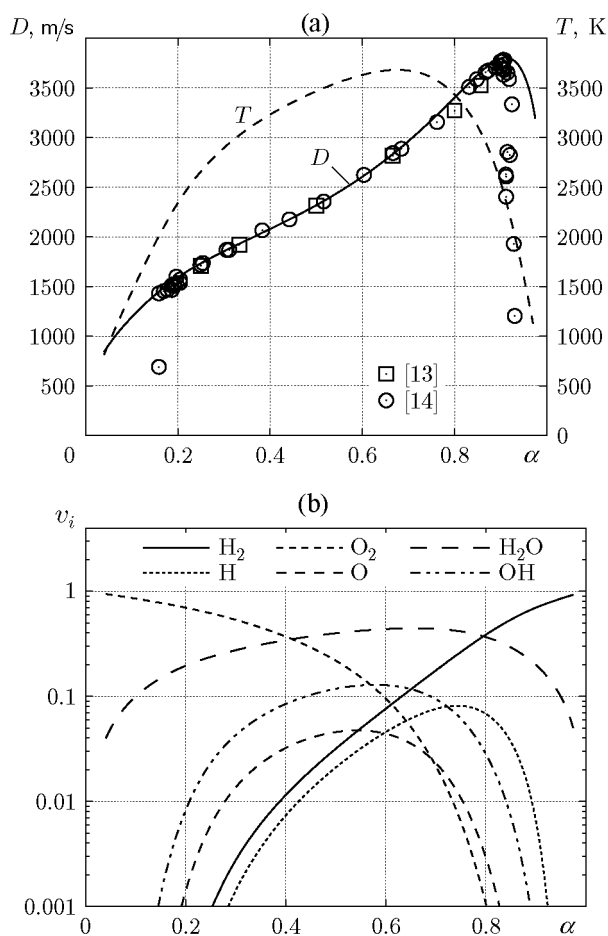


Fig. 7. Parameters of the Chapman–Jouguet detonation of the H_2 -based mixture: (a) wave velocity and temperature; (b) chemical composition.

detonation adiabat, the minimum velocity of the wave front D , and the condition $D = u + c$. For simplicity of numerical algorithm implementation, the latter criterion was used in the present study for determining the detonation parameters.

2.3. Comparisons with Experiments

For the tested models, the computed detonation velocities of the mixtures of α moles of the fuel and $1 - \alpha$ moles of the oxidizer (O_2) were compared with experimental data. The initial conditions for all compositions were the mixture temperature equal to 298.15 K and the pressure of 10^5 Pa.

In all figures, the curves show the data predicted by the models C_c (with possible formation of equilibrium vapors of carbon and condensed phase) and C_g (with forbidden formation of condensed carbon); the points are the experimental data.

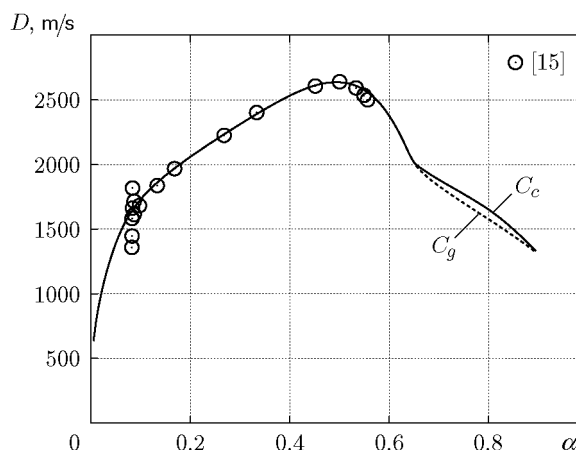


Fig. 8. Detonation velocity for the CH_4 -based mixture.

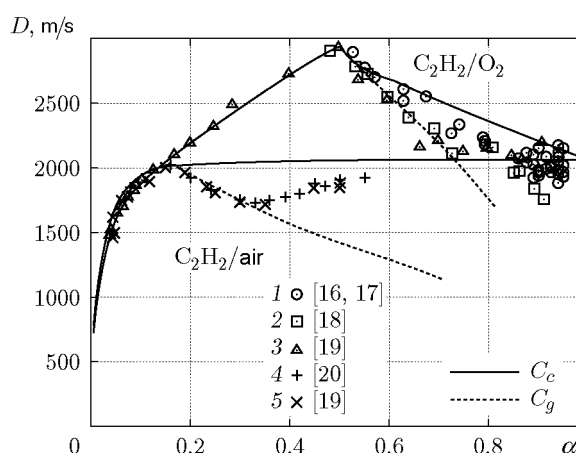


Fig. 9. Chapman–Jouguet detonation velocity for the C_2H_2 -based mixture: points 1–3 show the results for the mixture with oxygen, and curves 4 and 5 represent the data for the mixture with air.

Mixtures on the basis of H_2 (hydrogen) (Fig. 7). The computed velocities of the detonation wave agree well with the experimental measurements in a wide range of fuel concentrations, except for the flammability limits. Mixtures on the basis of CH_4 (methane) (Fig. 8). The computed velocities of the detonation wave agree well with the experimental measurements in a wide range of fuel concentrations, except for the flammability limits. In the domain of existence of detonation regimes, the equilibrium vapors of carbon and the condensed phase are not formed.

Mixtures based on C_2H_2 (acetylene) (Fig. 9). If the fuel fraction in the mixture is greater than 0.5, a significant amount of condensed carbon is released (Fig. 10a). In the case with forbidden formation of the condensed phase, carbon vapors are thermodynamically non-beneficial. The reaction products consist of the initial acetylene (Fig. 10b).

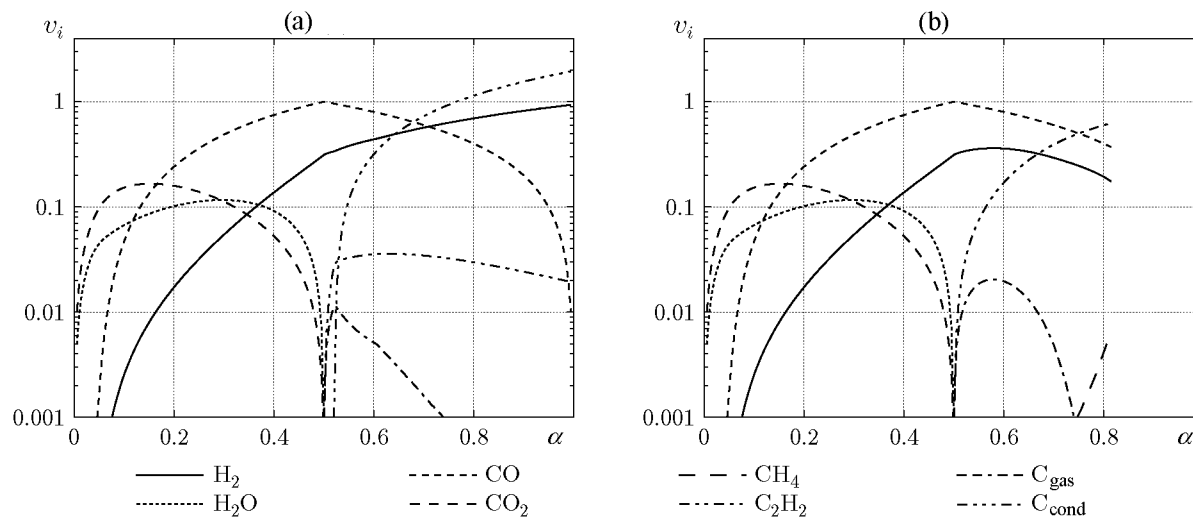


Fig. 10. Chemical composition at the Chapman–Jouguet point for the C_2H_2 -based mixture: (a) C_c model; (b) C_g model.

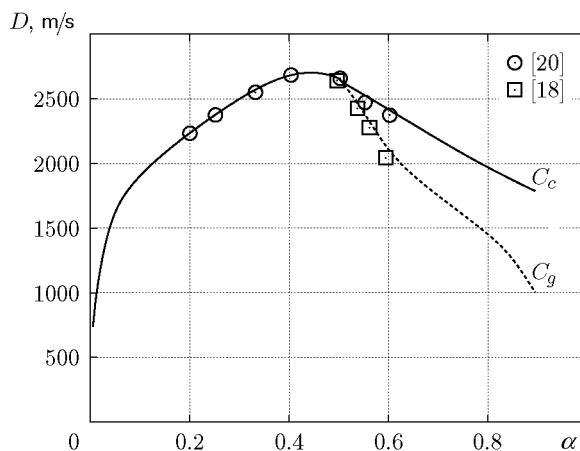


Fig. 11. Detonation velocity for the C_2H_2 -based mixture.

Acetylene stably detonates if there is a significant lack of oxygen. For C_2H_2 -based mixtures, comprehensive testing of the models with allowed and forbidden formation of equilibrium condensed carbon can be performed. Both models do not provide complete coincidence with the experiments and only identify the limits of the detonation parameters. The model with forbidden formation of condensed carbon ensures a slightly better description of the experimental data.

The development of a more comprehensive model that takes into account partial condensation of carbon would improve the description of the experimental data for acetylene, but it seems to be a premature event. In fact, only acetylene-based mixtures detonate under the conditions of formation of a significant amount of condensed carbon. For other combustible gases, the con-

centration limits of detonation do not allow one to study active formation of condensed carbon.

Mixtures based on C_2H_4 (ethylene) (Fig. 11). If the fuel fraction in the mixture is greater than 0.5, a significant amount of condensed carbon is released. In the case with forbidden formation of the condensed phase, carbon vapors are thermodynamically non-beneficial. Large amounts of acetylene and methane are formed in the reaction products. The model with forbidden formation of condensed carbon provides a slightly better description of the detonation velocity as a function of the fuel fraction in the initial mixture.

Mixtures based on C_3H_6 (propylene) (Fig. 12). If the fuel fraction in the mixture is greater than 0.4, a significant amount of condensed carbon is released. In the case with forbidden formation of the condensed

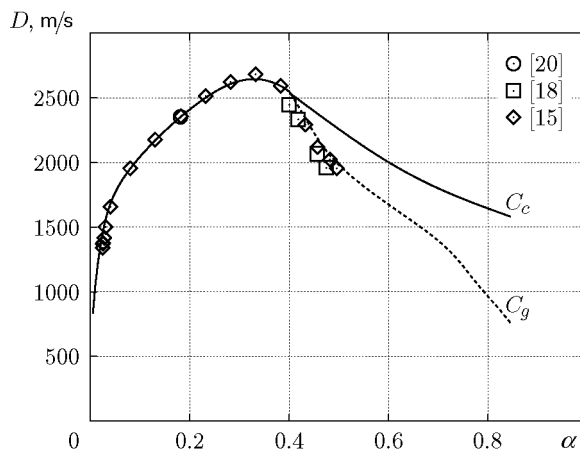


Fig. 12. Detonation velocity for the C_3H_6 -based mixture.

phase, carbon vapors are thermodynamically non-beneficial. Large amounts of acetylene and methane are formed in the reaction products. The model with forbidden formation of condensed carbon provides a slightly better description of the detonation velocity as a function of the fuel fraction in the initial mixture.

Mixtures based on C_3H_8 (propane) (Fig. 13). The fraction of condensed carbon in the detonation products in the domain within the concentration limits is small. Preference cannot be given to any of the models.

Mixtures based on C_4H_{10} (*n*-butane) (Fig. 14). The fraction of condensed carbon in the detonation products in the domain within the concentration limits is small. Preference cannot be given to any of the models.

Mixtures based on C_5H_{12} (pentane) (Fig. 15). The fraction of condensed carbon in the detonation products in the domain within the concentration limits is small. Preference cannot be given to any of the models.

Mixtures based on C_2N_2 (dicyan) (Fig. 16). There is no hydrogen in the composition. For this reason, record-beating detonation temperatures are reached (up to 6000 K), and there are no chemical compounds capable of binding gaseous carbon. Even under these conditions, the fraction of gaseous carbon is not high (less than 5% of all carbon in the mixture).

By virtue of the above-noted specific features, the detonation characteristics of dicyan-based combustible mixtures would probably be able to clarify the mechanism of carbon condensation in the explosion products. Unfortunately, because of incomplete coincidence of the models and experiments, we cannot give preference to any of the models.

3. BASIC RESULTS

A model of the equation of state for a reacting mixture of rarefied gases and a gas suspension of condensed species was developed by using methods of statistical physics. An *NVT* ensemble was considered for determining the detailed equilibrium chemical composition, and the minimum of the free energy for all possible species was found numerically. Knowing the chemical composition, one can calculate the pressure from the equation of state for an ideal gas and internal energy from the tabular dependence depending only on temperature.

Based on the algorithm described above, a software system was developed in the form of a library written in the C++ language and utilities with a web interface (<http://ancient.hydro.nsc.ru/chem>), which allows on-line computations of the thermodynamic parameters of reacting gases and a number of simple gas-dynamic flows, including detonation waves.

The software system has the following capabilities.

- Computation of the equilibrium chemical composition of the mixture of gases based on He, Ne, Ar, Kr, Xe, H, C, N, O, Al, Si, S, and Fe elements in a wide range of temperatures (for some species, in the interval from 200 to 20 000 K).
- Computation of a number of the thermodynamic parameters for specified temperature and density of the mixture: equilibrium chemical composition, pressure, enthalpy, internal energy, heat capacity, and equilibrium and frozen ratios of specific heats.
- Solution of the Hugoniot equation and construction of equilibrium and frozen shock adiabats.
- Determination of the thermodynamic parameters of combustion at $v = \text{const}$.

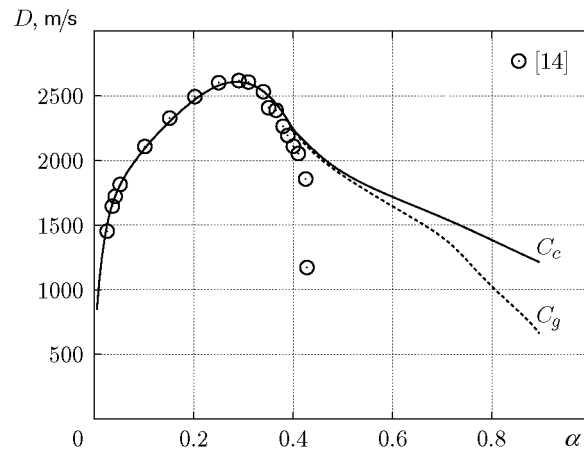


Fig. 13. Detonation velocity for the C_3H_8 -based mixture.

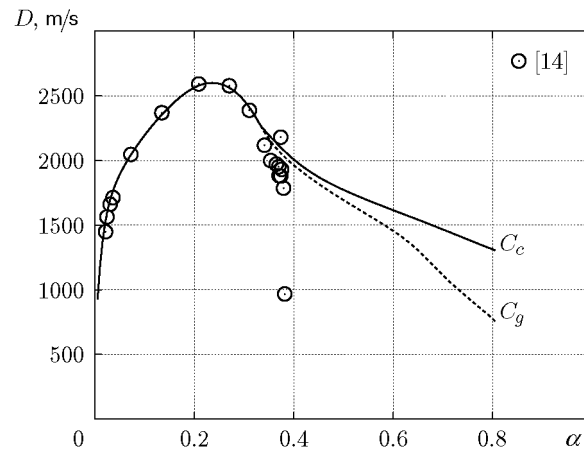


Fig. 14. Detonation velocity for the C_4H_{10} -based mixture.

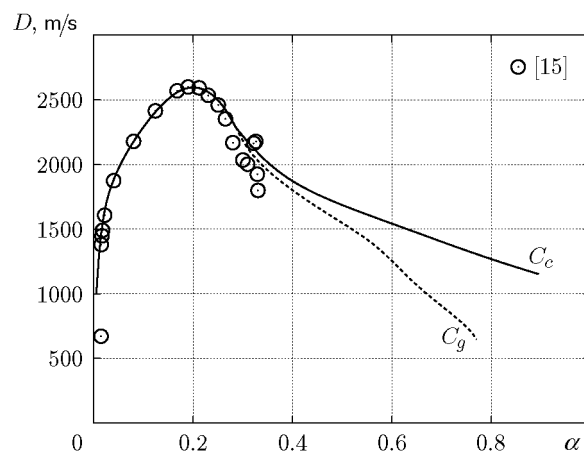


Fig. 15. Detonation velocity for the C_5H_{12} -based mixture.

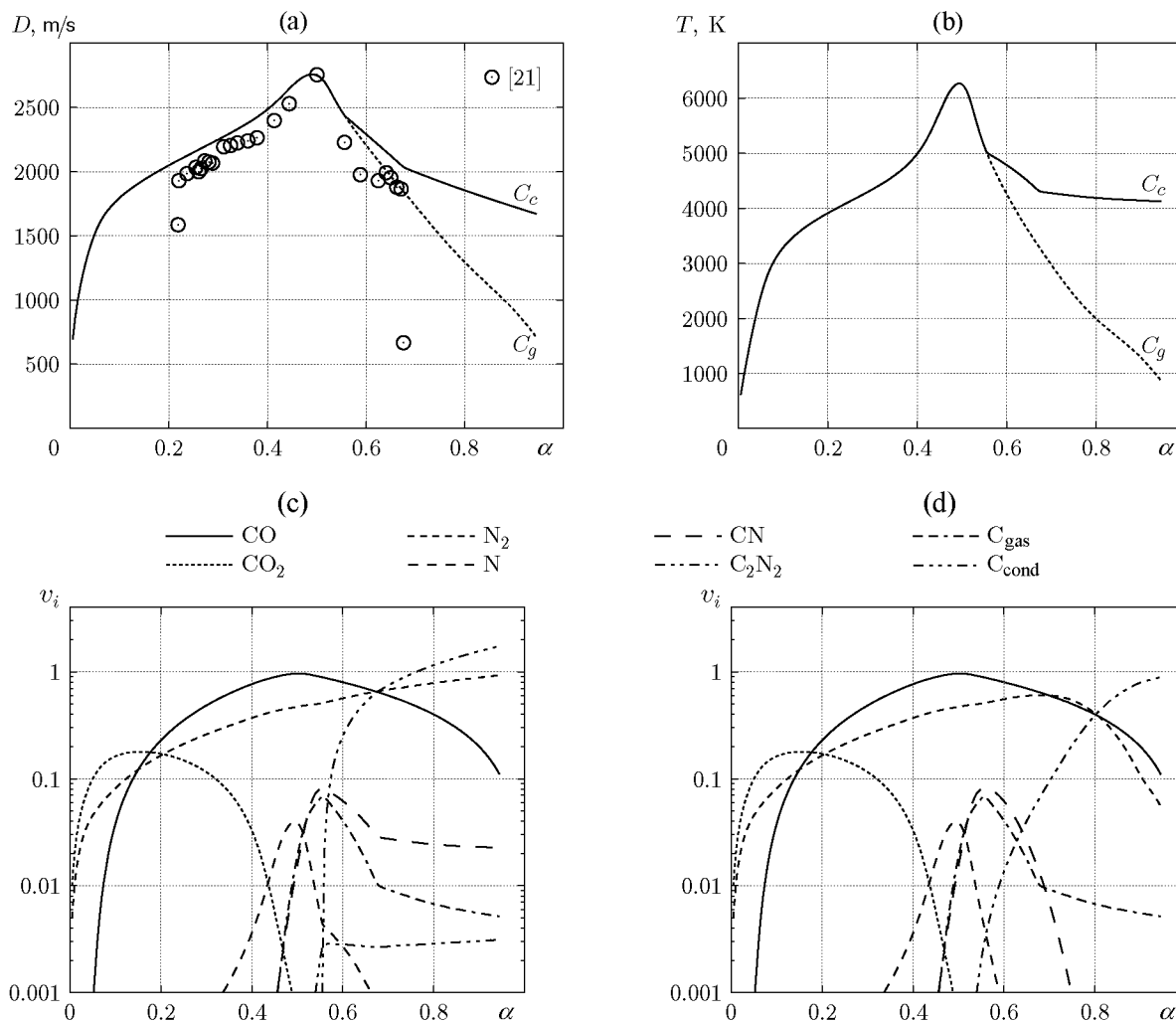


Fig. 16. Parameters of the Chapman–Jouguet detonation in the C_2N_2 -based mixture: (a) wave velocity; (b) temperature; (c and d) chemical composition calculated by the C_c model (c) and C_g model (d).

- Determination of the parameters of steady detonation waves.

- Allowance for the possibility of formation of condensed phases of C, H_2O , S, SiO_2 , Si, Fe, FeO, Fe_2O_3 , Fe_3O_4 , FeS, FeS_2 , Al, and Al_2O_3 .

The algorithm was tested through comparisons of the computed and experimental detonation velocities for a wide range of fuel–oxygen mixtures (H_2 , CH_4 , C_2H_2 , C_2H_4 , C_3H_6 , C_4H_{10} , C_5H_{12} , and C_2N_2). Good agreement is obtained in the case of oxygen excess and in the absence of condensed carbon in the explosion products.

For the majority of hydrocarbon fuels, the concentration limits do not allow considering steady detonation regimes with release of a significant amount of condensed carbon. An exception was acetylene-based mixtures with stable detonation in the case with a lack of

oxygen, for which none of the models provides an adequate description of the experimental data. A combined model with allowance for partial formation of the condensed carbon phase and additional experimental data will be needed to improve the description.

Available experimental data are more accurately described by the model with forbidden formation of condensed carbon.

REFERENCES

1. Yu. A. Nikolaev and M. E. Topchiyan, "Analysis of Equilibrium Flows in Detonation Waves in Gases," *Fiz. Goreniya Vzryva* **13** (3), 393–404 (1977) [*Combust., Expl., Shock Waves* **13** (3), 237–337 (1977)].
2. *Thermodynamic Properties of Individual Substances*, Ed. by V. P. Glushko, Vols. I–IV (Nauka, Moscow, 1978–1982) [in Russian].

3. *Thermodynamic Properties of Individual Substances*, Ed. by V. Iorish, Vols. V and VI; <http://www.chem.msu.su/Zn>.
4. G. V. Belov, S. A. Dyachkov, P. R. Levashov, et al., "The IVTANTHERMO-Online Database for Thermodynamic Properties of Individual Substances with Web Interface," *J. Phys.: Conf. Ser.* **946**, 012120 (2018); DOI: 10.1088/1742-6596/946/1/012120.
5. "Thermodynamic Properties of Individual Substances. IVTANTHERMO Database." <http://www.chem.msu.su/rus/handbook/ivtan>.
6. *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, Ed. by P. J. Linstrom and W. G. Mallard; DOI: 10.18434/T4D303; <https://webbook.nist.gov/chemistry>.
7. *Facility for the Analysis of Chemical Thermodynamics (FACT)*; <https://www.factsage.com>.
8. *Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications*; <https://cearun.grc.nasa.gov>.
9. G. Sanford and B. McBride, "Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications," *Tech. Rep. NASA* (1994); <https://ntrs.nasa.gov/citations/19950013764>.
10. L. D. Landau and E. M. Lifshits, *Theoretical Physics, Vol. V: Statistical Physics, Part 1* (Fizmatlit, Moscow, 2001; Pergamon Press, 1980) [in Russian].
11. D. Stull, E. Westrum, and G. Sinke, *The Chemical Thermodynamics of Organic Compounds* (Wiley, New York, 1969).
12. *GNU Scientific Library Reference Manual*, Ed. by M. Galassi et al.(2009); ISBN 0954612078; <http://www.gnu.org/software/gsl>.
13. A. A. Vasilev, A. I. Valishev, and V. A. Vasilev, "Detonation Hazards of Hydrogen Mixtures," in *Proc. of the Colloq. on Gas, Vapor, Hybrid and Fuel-Air Explosions*, pp. 392–395 (1998).
14. H. J. Michels, "Marginal Detonation in Hydrocarbon–Oxygen mixtures," Ph.D. Theses (Imperial College of Science, Technology, 1967).
15. H. J. Michels, G. Munday, and A. R. Ubbelohde, "Detonation Limits in Mixtures of Oxygen and Homologous Hydrocarbons," in *Proc. Roy. Soc. A* **319**, 461–477 (1970).
16. H. G. Wagner, "Soot Formation in Combustion," in *Proc. 17th Symp. (Int.) on Combustion (The Combustion Inst., Pittsburgh, 1979)*, pp. 3–19.
17. K. J. Dorge, F. Stephan, and H. G. Wagner, "Acetylene Detonations Hear the Upper Limit of Detonability," in *Proc. 17th Int. Colloquium on the Dynamics of Explosion and Reactive Systems (ICDERS-1999), July 25–30. Univ. Heidelberg IWR, 1999*.
18. I. S. Batraev, A. A. Vasil'ev, V. Yu. Ul'yanitskii, et al., "Investigation of Gas Detonation in Over-Rich Mixtures of Hydrocarbons with Oxygen," *Fiz. Goreniya Vzryva* **54** (2), 89–97 (2018) [*Combust., Expl., Shock Waves* **54** (2), 207–215 (2018)].
19. J. Breton, *Recherches Sur la Detonation des Melanges Gazeux: Theses Faculte des Sci.* (Univ. Nancy, 1936).
20. A. A. Vasil'ev and A. V. Pinaev, "Formation of Carbon Clusters in Deflagration and Detonation Waves in Gas Mixtures," *Fiz. Goreniya Vzryva* **44** (3), 81–94 (2008) [*Combust., Expl., Shock Waves* **44** (3), 317–329 (2008)].
21. G. Munday, A. R. Ubbelohde, and I. F. Wood, "Marginal Detonation in Cyanogenoxygen Mixtures," *Proc. Roy. Soc. A* **306** (485), 179–184 (1968).