Approximate Models of Chemical Kinetics for Detonation Processes in Mixtures of CH₄, H₂O₂ and O₃ with Air

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1 Introduction

The interest in detonation processes in gaseous mixtures containing methane, hydrogen peroxide and ozone has recently increased. Adequate understanding of these processes is necessary for solving problems of explosion safety in the mining and chemical industry and nuclear-power engineering. Numerical simulation of such processes needs the adequate models of chemical kinetics.

Typically the detailed system of equations of chemical kinetics is rather cumbersome, which significantly complicates the numerical analysis of gas-dynamic flows with chemical reactions. For instance, 2-D simulations of the wave of a multifront gas detonation using the detailed mechanism of the chemical reaction have been performed only for hydrogen-oxygen mixtures (see, for example, [1]). For such mixtures, the detailed mechanism of chemical reaction is comparatively simple. Because of the above-mentioned difficulties in the detailed description of the chemical reaction, approximate kinetic models are frequently used for numerical simulation of multifront detonation waves (see, for example, [2, 3]). In contrast with the reality, in the frames of such models the heat release of chemical reaction does not depend on pressure and temperature and molar mass and adiabatic index of gaseous mixture assume to be constant. There are no approximate kinetic models of detonation combustion of hydrogen peroxide- and ozone-air mixtures. Therefore there is still an urgent need to develop simple but highly accurate approximate kinetic models for detonation combustion of methane, hydrogen peroxide and ozone.

One of the most suitable approximate models of chemical kinetics in mixtures of hydrogen with oxygen, water vapor, and inert diluents is the model, presented in [4-7] (note this model as NFZT model). This model allows one to describe energy release and changes in thermodynamic parameters of the gas after the induction period with the help of one differential equation and several algebraic formulas. The calculation of the induction period of chemical reaction is not included in the framework of this model. The model is also applicable for calculating thermodynamic parameters of the gas in the chemical equilibrium state. Explicit algebraic formulas are obtained for such calculations [5-7]. The model is widely used to solve a wide range of research and application problems (for example, modeling of cellular structure of detonation waves [8], gas-droplet detonation [9], detonation application of coatings [10], pulse detonation engine [11], and explosion processes in bubble systems [12]). The objective of the present work is to develop two-step models of chemical kinetics of detonation combustion of methane-air mixtures and hydrogen-air mixtures with hydrogen peroxide and ozone additives. The models will be obtained by adapting the NFZT model for the mixtures under consideration.

2 Summary of NFZT model

NFZT is two-step model. The first step is induction period and the second one corresponds to main heat release. Note, that two-step model of chemical kinetic (including the induction step and the step of main heat release) for description of detonation processes in gaseous mixtures was used for the first time in [13].

In the frames of the NFZT model it is assumed that during induction period molar mass of a mixture remains constant and heat release of chemical reaction equals to zero.

After induction period (the second step of reaction) the model includes a kinetic equation for the molar mass of the gas

$$\frac{d\mu}{dt} = 4K_{+}\frac{\rho^{2}}{\mu}\left(1 - \frac{\mu}{\mu_{\text{max}}}\right)^{2} - AT^{3/4}(1 - \exp(-\Theta/T))^{3/2}\rho(\frac{\mu}{\mu_{\text{min}}} - 1)\exp(-E/\Re T)$$
(1)

and formulas for the specific internal energy of the mixture:

$$U(T,\mu) = U_{therm}(T,\mu) + U_{chem}(\mu), \qquad (2)$$

$$U_{therm}(T,\mu) = \left[\frac{3}{4}\left(\frac{\mu}{\mu_a} + 1\right) + \frac{3}{2}\left(\frac{\mu}{\mu_a} - 1\right)\frac{\Theta/T}{\exp(\Theta/T) - 1}\right]\frac{\Re T}{\mu},$$
(3)

$$U_{chem}(\mu) = E(\frac{1}{\mu} - \frac{1}{\mu_{\min}}),$$
 (4)

where ρ , *T* and μ are the density, temperature, and the mean molar mass of the gaseous mixture; *R* is the universal gas constant; μ_{a} , μ_{min} , μ_{max} are the molar masses of gas in the atomic, completely dissociated and completely recombined states; *A* and K_+ are the rate constants of dissociation and recombination of the generalized reaction products; θ is the effective excitation temperature of the vibrational degrees of freedom of the molecules; *E* is the mean dissociation energy of the reaction products; *U* is the total specific internal energy of the gas, U_{therm} and U_{chem} are thermodynamic and chemical parts of *U*; *t* is the time. The algorithm for calculation constants μ_{a} , μ_{min} , μ_{max} , *A*, θ , *E* is presented in [5, 6, 14].

The first and second terms in (1) correspond to recombination and dissociation reactions.

The model takes into account that the energies of dissociation of diatomic molecules (H_2 , O_2 , OH) into atoms are approximately equal to the energy of dissociation of H_2O molecule into OH and H. Thus, the recombination reaction heats are assumed to be identical and noted as *E*.

It is known that recombination reactions in hydrogen-oxygen mixtures occur almost without the activation energy. Therefore, the activation energy of recombination reactions in the model is assumed to be zero. As a result, the first term in (1) has no exponent. The activation energy in the second term in (1) equals E. The reason is that the difference between the activation energy of the dissociation reaction and that of the reverse recombination reaction equals the chemical reaction heat.

For a specified caloric equation of state (2-4), the rate constants of direct and reverse chemical reactions in (1) cannot be arbitrary but should be correlated with allowance for the second law of thermodynamics. Therefore, the form of the temperature-dependent preexponent of the dissociation rate constant was obtained from the condition that thermodynamic potentials of the gas have an extremum in chemical equilibrium $(d\mu/dt = 0)$.

The recombination rate constants differ from each other insignificantly. In the kinetic model, therefore, they are assumed to be identical and equal to K_+ . Formula (3) was derived by analyzing the mean number of degrees of freedom of molecules versus temperature. Formula (4) is based on the assumption that the dissociation energy of diatomic molecules and the energy of dissociation of H₂O molecule into OH and H equal to *E*.

The NFZT model can also be used to calculate thermodynamic parameters of the gas in chemical equilibrium $(d\mu/dt = 0 \text{ in } (1))$.

Thus, the NFZT model has some principal advantages. The model is physically grounded; all constants of the model have a physical meaning. It is simple and highly accurate. The model is consistent with the second law of thermodynamics and with the le Chatelier principle.

The NFZT model cannot be directly (without appropriate adaptation) used to calculate detonation processes in mixtures containing methane, hydrogen peroxide and ozone for the following reasons. Equation (1) holds only after the induction period (for theoretical modeling of the wave of multifront gas detonation it is necessary to describe the whole process of chemical transformation of the mixture, including the part inside the induction zone). Additionally, (1-4) are valid for no more than triatomic molecules (CH_4 , and H_2O_2 molecules are not triatomic).

The algorithm for adaptation of the NFZT model to calculating the gas-detonation processes in mixtures containing methane, hydrogen peroxide and ozone are presented in Sections 2 and 3.

2 The model of chemical kinetics in methane-based mixture

We consider a methane-air mixture a_1 CH₄ + a_2 O₂+ a_3 N₂, $2a_2 \ge a_1$. Without loss of generality, we can assume that $a_1 = 1$.

As is commonly done, we calculate the value of the induction parameter *Y* during the induction period of the chemical reaction in the gas mixture with variable pressures and temperatures by the formula:

$$Y = \int_{0}^{t_i} \frac{dt}{\tau_i} \quad , \tag{5}$$

where τ_i is the induction period at constant parameters. At the beginning of the induction period, Y = 0, and at the end of it (the moment in time $t = t_i$), Y = 1. Semi-empirical relations have to be used to calculate τ_i . The value of τ_i for the methane–air mixture will be calculated, for example, by the formula, recommended in [15] as the best for calculations of the cell size of the detonation wave.

We replace the real multistep process occurring during the induction period with some overall reaction chosen from the following general considerations. We take into account that by the end of the induction period, the temperature increase (and, hence, the total heat release due to chemical reactions) is low. Therefore, the overall reaction is chosen so that its thermal effect is much smaller than the maximum possible thermal effect of the complete recombination of the reaction products to form CO_2 and H_2O molecules. Note that under this condition, the thermal effect of the overall reaction will also be much smaller than the thermal effect at the Chapman–Jouguet point.

We also take into account that the induction period involves chemical reactions leading to the formation and increase in the number of active centers and decomposition of heavy molecules. In our case, the heavy molecules are methane molecules. It is therefore assumed that during the induction period, all methane molecules decompose to form CO molecules. C atoms in the products of the overall reaction are neglected since the mixture contains a more than sufficient amount of oxidizer.

Thus, we assume that during the induction period, each methane molecule of the mixture is involved in the chemical reaction $CH_4 + O_2 \rightarrow CO + OH + 1.5H_2$. It is easy to show that the thermal effect of this reaction is significantly smaller than the maximum possible thermal effect of the chemical reaction per one mole of CH₄. Thus, this overall reaction most accurately satisfies the above conditions.

Let β be the fraction of un-decomposed methane. In the initial state, $\beta = 1$; during the induction period, β decreases monotonically; and at the end of the induction period, $\beta = 0$. According to the chemical decomposition of methane molecules described above, the chemical composition of the a_1 CH₄ + a_2 O₂+ a_3 N₂ mixture for $a_2 \ge 1$ can be written as follows: β CH₄ + $(1 - \beta)CO + (1 - \beta)OH + (1.5 - 1.5\beta)H_2 + (a_2 - 1 + \beta)O_2 + a_3N_2$.

We note that the value of β affects only the wave parameter profiles in the induction zone. The wave velocity, flow parameters at the Chapman-Jouguet point, and zone of main heat release do not depend on β . Therefore, if the above conditions are satisfied, the particular form of the formula for calculating

 β affects the wave parameter profiles in the induction zone only quantitatively. As a rule, the chemical reaction rate increases at the end of the induction period. It is therefore reasonable to choose a formula for calculating β that it meets the above conditions, and the rate of decrease as the movement grew mixture in the induction zone. For example, the quantity β can be defined as

$$\beta = (e^{\alpha} - e^{\alpha Y}) / (e^{\alpha} - 1),$$

where the constant $\alpha > 1$. Within this kinetic model, the chemical composition of the gas during the induction period is calculated by explicit algebraic formulas. Therefore, the molar mass and the internal energy of the gas can be easily calculated by the well-known standard algorithms using the thermodynamic parameters of individual species.

In the frames of the proposed model the mixture after induction period is not more than triatomic and all assumptions of NFZT model are valid. Thus, the second step involving the zone of main heat release can be described by equation (1) and formulas (2-4).

The proposed approximate kinetic model is closed and suitable for calculating the molar mass and internal energy of the mixtures needed for numerical calculations of the parameters and two-dimensional structure of the detonation wave.

3 Two-step models of chemical kinetics in hydrogen-air mixtures with ozone and hydrogen peroxide additives

Let's consider the mixture $a_1H_2O_2 + a_2H_2 + a_3O_2 + a_4H_2O + a_5N_2$, $a_2 \ge a_1$. Duration of the first step of chemical reaction can be calculated by equation (5). We formally assume that the molar mass of the gas remains unchanged during this step. We also assume that the composition of the gas mixture continuously transforms so that the mixture contains no more than triatomic molecules by the moment in time $t = t_i$. In addition, hydrogen peroxide decomposition is assumed to proceed so that an H₂O molecule is formed from each H₂O₂ molecule, and the oxygen atom joins a H₂ molecule present in the mixture to form a water molecule. Thus, the initial mixture transforms during the induction period into the mixture $b_1H_2 + b_2O_2 + b_3H_2O + b_4N_2$. Stoichiometric coefficients b_i can be easily calculated from the system of algebraic equations of atomic balance and condition $\mu = \text{const}$ during induction period. As in case of methane/air mixture, it is possible to introduce the fraction of un-decomposed hydrogen peroxide and use the formula for calculation β , presented above.

After complete decomposition of hydrogen peroxide, described above, all assumptions of the NFZT model are valid, and formulas (1-4) can be used for description the second step of chemical reaction. Note, that in the frames of this model both steps of chemical reaction are not thermally neutral.

Like in case of hydrogen peroxide mixture with air, similar approach can be used for description of chemical reaction in ozone-air mixture. The first step is associated with the reaction of ozone molecules according to the overall reaction $O_3 + H_2 \rightarrow O_2 + H_2O$, the second step is associated with the combustion of most of the hydrogen.

4 Numerical modeling of multi-front detonation waves in methane-air mixtures and hydrogen-air mixtures with hydrogen peroxide additives

We used the presented models of chemical kinetics for 2-D modeling of parameters and cellular structure of detonation waves in methane-air mixtures and hydrogen-air mixtures with hydrogen peroxide additives. Some typical results are shown in Figures 1-3.

Note, that the presented models of chemical kinetics, allow us to describe non-regular structure of detonation wave in CH_4 -air mixture and two-scale (bifurcation) structures of detonation wave in H_2O_2 -air mixtures. Calculated value of cell size in methane-air mixture (33 cm) is very good corresponds to the experimental data [15]. The calculated results of the detonation cell width in mixtures with hydrogen peroxide demonstrate a good (better than 10%) quantitative agreement with corresponding

results, obtained in the frames of the generally accepted analytical model of detonation cell, presented in [16].



Figure 1. Numerical Schlieren-visualization of detonation wave structure in stoichiometric methane-air mixture at normal conditions in 40-cm wide channel; x (cm), y(cm).

Figure 2. Temperature (in K) map of the flow field of DW propagating in $2H_2+O_2+7Ar+1.11 H_2O_2$ mixture in 0.64-cm wide channel, $P_0=0.2$ atm.



Figure 3. Two-dimensional (bifurcation) cellular structure of detonation wave (numerical soot tracks) in $2H_2 + O_2 + 7Ar + 1.11 H_2O_2$ mixture in 2.5-cm wide channel, $P_0 = 0.066$ atm.

4 Conclusions

The approximate two-step models of chemical kinetics in methane-air mixtures and hydrogen-air mixtures with hydrogen peroxide and ozone additives are presented. Advantages of the models are their simplicity, lack of arbitrariness in the choice of the constants, consistency with the second law of thermodynamics, and high accuracy. The models do not impose stringent requirements to computer performance and memory, as simulation with a detailed kinetic mechanism does. The models are verified in corresponding numerical calculations of parameters and cellular structure of detonation waves. These models provide accurate calculations of the parameters and structure of detonation waves. This work was financially supported by Russian Foundation for Basic Researches (Grant № 11-01-00634a) and by the Program of Basic Researches № 26.2 "Combustion and Explosion" of the Presidium of the Russian Academy of Sciences.

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