

ANALYSIS OF THE EFFECT OF MATHEMATICAL MODELS OF CHEMICAL TRANSFORMATIONS ON THE IGNITION OF HYDROGEN-OXYGEN MIXTURES

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This paper presents an analysis of the influence of mathematical models of chemical transformation on the combustion of hydrogen-oxygen mixtures. The results of the analysis show that, despite the widespread use of hydrogen combustion processes for practical purposes and a fairly large number of publications, the development of kinetic schemes for hydrogen combustion is still relevant at the present time. In this work, using the example of solving the problem of determining the induction period of combustion of a hydrogen-oxygen mixture in an adiabatic reactor, we test various kinetic schemes of hydrogen combustion: two one-stage schemes consisting of sixteen reactions. It is shown that the most accurate description of the experimental data on the delay times of an adiabatic explosion can be obtained using a more complex kinetics of hydrogen oxidation, and the simplification of the mechanism to one overall reaction is suitable only for approximate estimates.

Keywords: mathematical modelling; combustion and explosion; period of occurrence.

Introduction

Currently, much attention is paid to the search and development of energy production technologies that do not have a polluting effect on the environment and structural elements. One of the actively developed areas is hydrogen energy, which involves the use of hydrogen as the main means of generating energy. This direction is actively developed and implemented in the creation of new models of rocket technology. However, the high chemical activity in combination with a rather low concentration combustion limit and other characteristics of the substance imposes a number of safety requirements at all stages of the industrial use of hydrogen.

In addition, the results of experimental studies of processes associated with hydrogen combustion on a reduced scale cannot be fully used to describe full-scale processes, and full-scale experiments can be difficult due to the high fire and explosion hazard. To study such processes, it is necessary to use mathematical modelling methods.

Mathematical modelling of flows of multicomponent and multiphase continuous media is widely used in various branches of science and technology and, at times, is the only reliable way to analyze the occurrence of emergency situations in the case of fast processes. The development of high-performance computing technology makes it possible to construct more and more complex mathematical models for describing fast processes in multicomponent media.

A mathematical model of a multicomponent mixture, taking into account chemical transformations in the approximation of a continuous media, is a system of equations

based on the laws of conservation of mass, momentum and phase energy, and can only be solved numerically using an approach that makes it possible to reasonably apply splitting by physical processes. Splitting by physical processes consists in dividing the calculation of the parameters of chemical transformations and hydrodynamic processes into two separate stages. In this case, the influence of chemical transformations on hydrodynamic processes is taken into account in the form of source terms in the equations for the conservation of the energy of the mixture and the mass fractions of the components. The chemical transformations themselves can be described using a system of equations of chemical kinetics.

Despite the fact that the reactions of oxidation (combustion) of hydrogen and methane are very widely used for practical purposes, and there exists a fairly large number of publications, the development of kinetic schemes for the combustion of hydrogen and methane is still relevant at the present time. Therefore, the purpose of this study is to analyze the influence of mathematical models of chemical transformations on the dynamics of energy release during the combustion of hydrogen-oxygen mixtures.

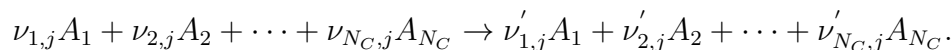
1. Mathematical Model of Chemical Transformations in Adiabatic Reactor

One of the simplest and most effective ways to study the effect of mathematical models of chemical transformation on the combustion of hydrogen-oxygen mixtures is to determine the adiabatic explosion delay (induction period).

Consider an *adiabatic reactor* that is a reactor in which there is no heat and mass exchange with the environment, therefore, all the heat obtained in the course of exothermic oxidation reactions is used to heat up the system. In such a system, under any initial conditions, the heat released during the reactions leads to a progressive heating of the mixture, which ends in a thermal explosion. The time interval from the beginning of the process to the moment of a sharp increase in temperature is called the adiabatic induction period (*combustion delay*) t_{ad} . The duration of the induction period depends both on the initial conditions and on the thermophysical properties of the mixture and the parameters of the chemical reaction (rate constant, activation energy, thermal effect). During the process, the chemical composition of the reacting mixture and its temperature change. At the initial time $t = 0$, the following parameters are specified: the initial temperature T_0 , the pressure P_0 ; the composition of the mixture is determined by the set of initial mole fractions of the components.

Since the system is ideally isolated, the gradients of concentration, temperature, and pressure are zero on the reactor walls. The consequence of this is the absence of gradients throughout the entire process, i.e. concentrations, temperature and pressure change synchronously at all points of the reacting mixture.

Consider a closed adiabatic reactor of constant volume that contains a mixture of gases of variable composition from N_C components participating in N_R elementary chemical reactions. We write the j -th reaction as the generalized stoichiometric equation:



Here A_k is the chemical symbol of the k -th substance (for example, H_2 , CO_2 , O_2 , H , O , etc.), $\nu_{k,j}$ is the stoichiometric coefficient of the k -th substance in the j -th reaction, which

indicates the number of moles (or molecules) of the given reagent that enters the reaction as the initial substance, and $\nu'_{k,j}$ is the number of moles resulting from the reaction. The stoichiometric coefficients of substances not participating in the j -th reaction are equal to 0.

The rate of the j -th reaction in the gas phase is determined by the law of mass action (dependence on concentrations) and the Arrhenius law (dependence on temperature) and can be expressed as follows [1]:

$$W_j = k_{0j} T^{b_j} \exp\left(-\frac{E_j}{RT}\right) \prod_{k=1}^{N_C} C_k^{\nu_{k,j}},$$

where k_{0j}, T^{b_j}, E_j are the kinetic constants for calculating the rate of the j -th reaction, R is the universal gas constant. The quantities k_{0j} of bimolecular and trimolecular reactions have the dimensions $m^3 \cdot mol^{-1} \cdot s^{-1}$ and $m^6 \cdot mol^{-2} \cdot s^{-1}$, respectively, and the activation energy E_j is $J \cdot mol^{-1}$.

The mathematical model of the adiabatic reactor is described by the energy balance equation for determining the temperature T of the reacting mixture and N_C equations for the molar concentrations C_k of each of the reagents [2,3]:

$$\frac{dT}{dt} = - \sum_{k=1}^{N_C} h_k \frac{dC_k}{dt} / \sum_{k=1}^{N_C} c_{P_k} C_k,$$

$$\frac{dC_k}{dt} = \sum_{j=1}^{N_R} W_j (\nu'_{k,j} - \nu_{k,j}), k = 1, 2, \dots, N_C,$$

where t is the time, h_k is the total specific molar enthalpy (J/mol), c_{P_k} is the isobaric molar heat capacity ($J/(K \cdot mol)$). The current mixture pressure can be calculated using the formula:

$$p = RT \sum_{i=1}^{N_C} C_i.$$

The heat capacity at constant pressure c_P and the total enthalpy h of each substance are calculated using approximation dependencies on temperature [4]:

$$h(T) = \Delta h^0(0) + [h^0(T) - h^0(0)],$$

$$[h^0(T) - h^0(0)] = T(a_1 - 2a_2 X^{-2} - a_3 X^{-1} + a_4 X + 2a_5 X^2 + 3a_6 X^3), (J/mol),$$

$$c_P(T) = a_1 + 2a_2 X^{-2} + 2a_4 X + 6a_5 X^2 + 12a_6 X^3, (J/(K \cdot mol)), X = \frac{T}{10000},$$

where a_i are the coefficients of the polynomial for each substance, $\Delta h^0(0)$ is the standard enthalpy of formation of the substance at $T = 0$. In this mathematical model, the thermal effect is taken into account in accordance with the Hess law, which makes the model more correct.

To solve the problem of determining the induction period, this system must be supplemented with the initial conditions for the concentrations and temperature of the gas mixture: $t = 0, T = T_0, C_k = C_{0k}$.

Therefore, the problem of determining the induction period and analyzing the influence of mathematical models of chemical transformations on the dynamics of energy release during the combustion of hydrogen-oxygen mixtures is reduced to solving a system of ordinary differential equations. This system of ordinary differential equations is very complicated even for numerical integration, since during the process described by these equations, the rates of concentration and temperature growth change very strongly, which makes the system unsolvable by simple explicit methods (the stiffness coefficient reaches 10^{12}). The problem of solution instability can be avoided by using the so-called implicit solution methods. Another way to avoid this problem is to eliminate fast stages by splitting the time scales. A detailed analysis of methods for solving systems of stiff differential equations is carried out in [5].

In this study, to solve a system of stiff differential equations of chemical kinetics, we use the built-in MatLab ode15s method, which implements the implicit Gear method of a variable order of accuracy. The accuracy of calculations directly depends on the parameters of the built-in solver, so the correct selection of the adaptive step, as well as setting the calculation error, plays an important role [6].

As the analyzed mathematical models of chemical transformations, we select models based on 16 chemical reactions, the rate constants of which are given in Table 1 (8 reversible reactions, 6 components) [7]: H_2, O_2, H_2O, H, O, OH , as well as two one-step mechanisms of hydrogen oxidation [8]: $2H_2 + O_2 = 2H_2O$, where, in the first case, the rate constants of chemical transformations are presented as:

$$k_1 = 2, 14 \cdot 10^8 \exp\left(-\frac{129000}{RT}\right), [k] = \frac{m^3}{mol \cdot s}, [E] = \frac{J}{mol},$$

and in the second case the constants are presented as follows:

$$k_2 = 2, 96 \cdot 10^5 \exp\left(-\frac{6900}{RT}\right), [k] = \frac{m^3}{mol \cdot s}, [E] = \frac{J}{mol}.$$

Table 1

Kinetics of hydrogen oxidation from 16 reactions [7]

No.	Reaction scheme	Direct reaction			Reverse reaction		
		k_0	b	E/R	k_0	b	E/R
1,2	$H + O_2 = OH + O$	3.0e8	0	8810	2.48e7	0	660
3,4	$O + H_2 = OH + H$	3.0e8	0	4030	1.3e7	0	2490
5,6	$OH + H_2 = H_2O + H$	3.0e8	0	3020	1.33e9	0	10950
7,8	$2OH = H_2O + O$	3.0e8	0	3020	3.12e9	0	12510
9,10	$H_2 + M = 2H + M$	1.85e14	-1	54000	1.0e4	0	0
11,12	$H_2O + M = H + OH + M$	9.66e15	-1	62200	1.0e5	0	0
13,14	$OH + M = O + H + M$	8.0e13	-1	52200	1.0e4	0	0
15,16	$O_2 + M = 2O + M$	5.8e13	-1	60600	6.0e2	0	0

2. Results

Figs. 1 and 2 show the dependence of the combustion period on the initial temperature of oxygen-hydrogen mixtures and compare the calculations with the experimental data of the works [9,10]. The initial values of the concentrations are $H_2 = 0.6667$, $O_2 = 0.3333$ (in mole fractions) and the mixture pressure is $P_0 = 1$ atm. All components with equal probability are chosen as the third particle.

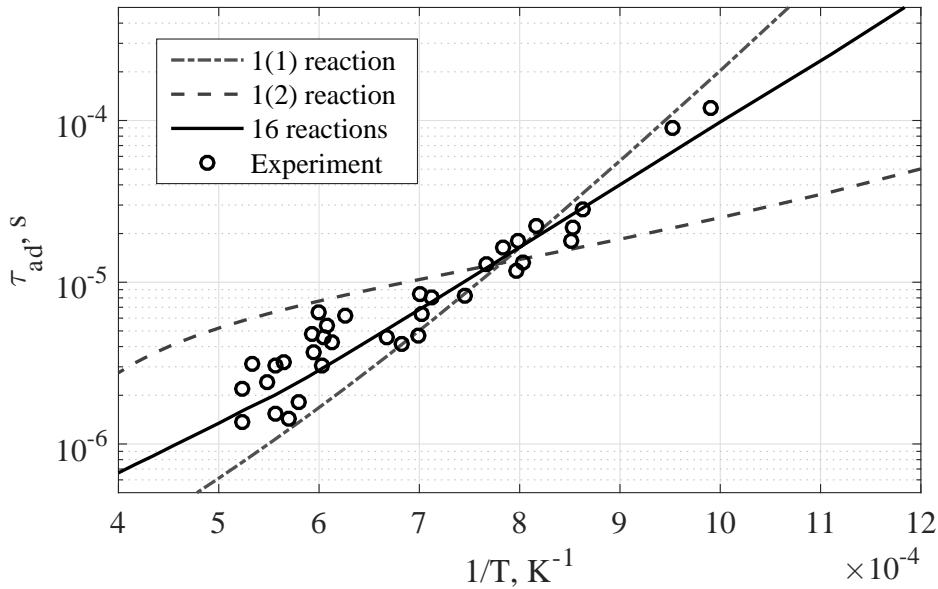


Fig. 1. Dependence of the combustion period on temperature [9]

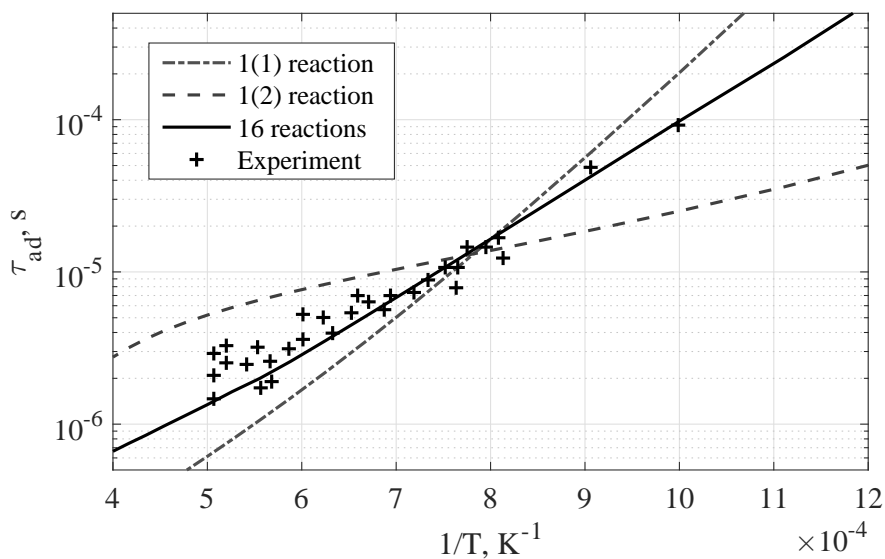


Fig. 2. Dependence of the combustion period on temperature [10]

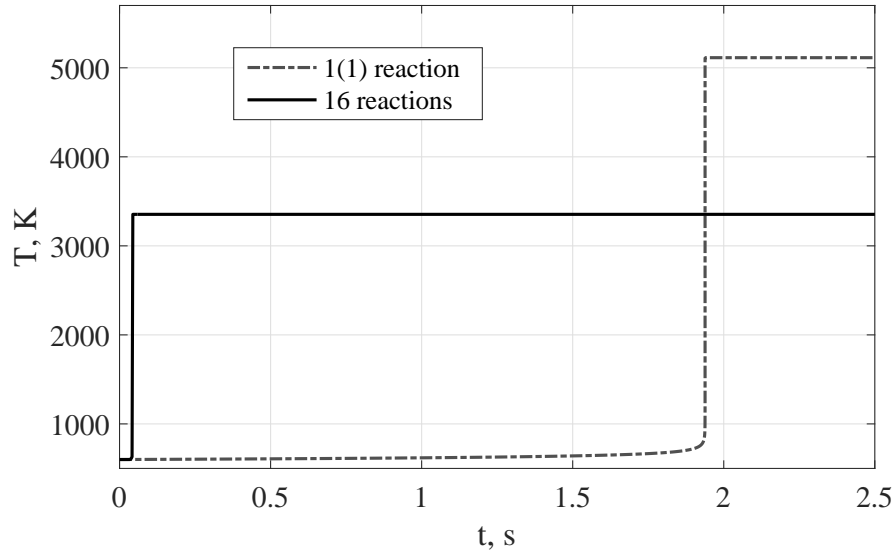


Fig. 3. Time dependence of temperature for various mechanisms and reaching the stationary state at $P_0 = 1$ atm, $T_0 = 600$ K

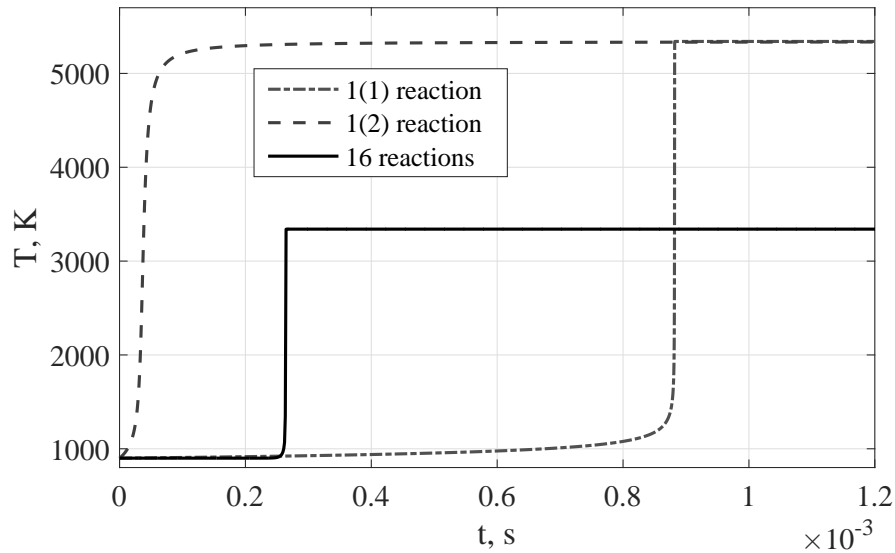


Fig. 4. Time dependence of temperature for various mechanisms and reaching the stationary state at $P_0 = 1$ atm, $T_0 = 900$ K

The dependencies of the induction period of the adiabatic explosion on temperature, presented in Figs. 1 and 2, show that the best agreement with experiment can be achieved only for a mathematical model of chemical transformations, which includes 16 reactions.

Another effective way to study the effect of mathematical models of chemical transformation on the combustion of hydrogen-oxygen mixtures is to determine the energy characteristics (for example, the combustion temperature of hydrogen-oxygen mixtures) after reaching the stationary regime of operation of an adiabatic reactor. Figs. 3-5

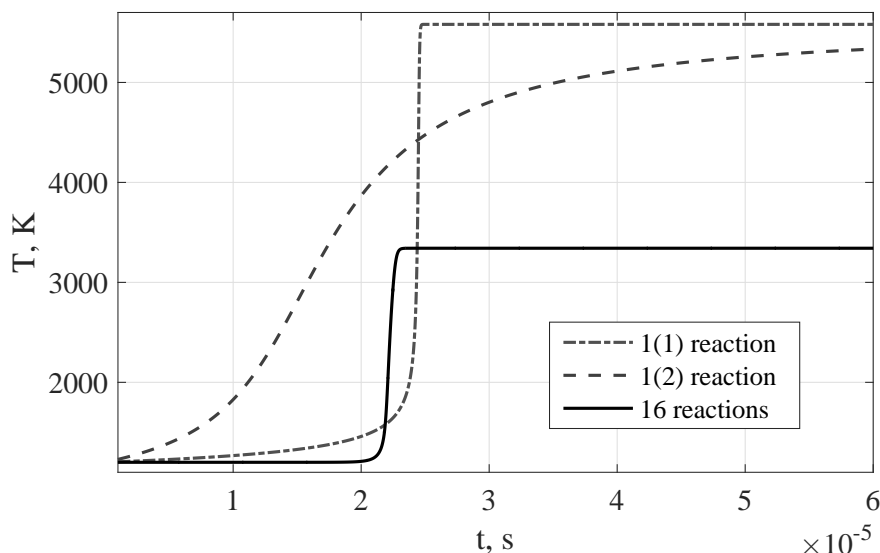


Fig. 5. Time dependence of temperature for various mechanisms and reaching the stationary state at $P_0 = 1$ atm, $T_0 = 1200$ K

show the time dependencies of temperature for various kinetic mechanisms when an adiabatic reactor reaches the stationary state. Table 2 presents the values of pressure and temperature of the mixture after the reactor reaches the stationary state for three mathematical models of chemical transformation.

Table 2

Pressure and temperature of the mixture after reaching the stationary state

T_0, K	1 reaction (1)		1 reaction (2)		16 reactions	
	p, Pa	T, K	p, Pa	T, K	p, Pa	T, K
600	575699.99	5113.67	575617.26	5112.39	456267.85	3353.96
800	444439.74	5263.67	443782.04	5249.99	346614.33	3343.01
900	400840.75	5340.72	400226.80	5326.34	310300.43	3340.71
1000	366063.29	5419.28	365675.16	5409.16	281361.10	3339.87
1200	314165.36	5581.16	309783.48	5443.76	238184.02	3341.46
1500	262831.15	5836.51	258766.28	5676.60	195378.58	3349.35
1800	229193.27	6107.44	225291.48	5922.77	167136.26	3361.32
2000	212670.72	6296.84	208844.98	6095.38	153137.75	3370.75
2200	199366.22	6493.21	195601.98	6274.90	141762.82	3381.00
2500	183743.84	6800.46	180055.53	6556.90	128229.01	3397.46

Conclusion

The calculation results presented in Figs. 3–5 and Table 2 show that mathematical models of the chemical transformation of hydrogen-oxygen mixtures, based on one-stage mechanisms of hydrogen oxidation, when reaching the stationary regime, give mixture temperature values that do not agree with known experimental data.

Analysis of the influence of mathematical models of chemical transformation on the combustion of hydrogen-oxygen mixtures, carried out in the work, allows us to conclude that only a mathematical model of chemical transformation for hydrogen-oxygen mixtures, constructed on the basis of 16 chemical reactions, allows obtaining results consistent with experiment.

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АНАЛИЗ ВЛИЯНИЯ МАТЕМАТИЧЕСКИХ МОДЕЛЕЙ ХИМИЧЕСКИХ ПРЕВРАЩЕНИЙ НА ВОСПЛАМЕНЕНИЕ ВОДОРОД-КИСЛОРОДНЫХ СМЕСЕЙ

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В данной работе представлен анализ влияния математических моделей химического превращения на воспламенение водород-кислородных смесей. Результаты проведенного анализа показывают, что, несмотря на широкое применение процессов горения водорода в практических целях и достаточно большое количество публикаций, разработка кинетических схем горения водорода является актуальной и в настоящее время. На примере решения задачи об определении периода индукции воспламенения водород-кислородной смеси в адиабатическом реакторе в работе были апробированы различные кинетические схемы горения водорода: две одностадийные схемы, схема, состоящая из шестнадцати реакций. Было показано, что наиболее точное описание экспериментальных данных по временам задержки адиабатического взрыва удастся получить, используя более сложную кинетику окисления водорода, а упрощение механизма до одной брутто-реакции пригодно только для приблизительных оценок.

Ключевые слова: математическое моделирование; горение и взрыв; период индукции.

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