Technical Physics, 2023, Vol. 68, No. 8

03

Vibrational nonequilibrium in the reaction of hydrogen with oxygen (Review)

© O.V. Skrebkov, S.S. Kostenko, A.L. Smirnov

Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry, Russian Academy of Sciences,
142432 Chernogolovka, Russia
e-mail: asm@icp.ac.ru

Received March 27, 2023
Revised June 13, 2023
Accepted June 13, 2023

The field of research of vibrational relaxation processes in their interaction with chemical reactions is currently characterized by high activity. This review is based on our work. A vibrational nonequilibrium model of hydrogen oxidation is presented within the framework of a sequential elementary kinetic approach. The central element is to take into account the vibrational nonequilibrium of the HO_2 radical as the most important intermediate in the process of chain branching and in the formation of electronically excited particles. The results of shock wave experiments and corresponding calculations for the H_2+O_2+Ar system at temperatures $T < 1500\,K$ and pressures $p < 4\,atm$ are discussed. It is shown that under these conditions, vibrational nonequilibrium is the most important factor determining the mechanism and rate of the process. The analysis of the thermal effect at various stages of the process, the inhibition of the reaction of hydrogen with oxygen by additives of polyatomic gases and the mechanism of formation of an electronically excited $OH(A^2\Sigma^+)$ radical is given.

Keywords: chemical kinetics, vibrational relaxation, electronic excitation, shock wave.

DOI: 10.61011/TP.2023.08.57259.39-23

Introduction

A wide class of problems that require taking into account the kinetics of energy exchange processes between different degrees of freedom of molecules is the subject of numerous studies, from the middle of the last century to the present time (see, for example, [1–38]). This class of problems should include the processes of combustion, detonation, gas flows behind shock waves, including shock waves in front of a hypersonic vehicle under conditions of entry into the atmosphere of the Earth and other planets [1,2,7–33], flows in nozzles, including flows in the nozzles of rocket engines, gas-dynamic or chemical lasers [3–6,34–38].

When thermodynamic equilibrium is violated and subsequently established through molecular collisions, excitation (or deactivation) of all degrees of freedom (translational, rotational, vibrational and electronic), as well as chemical transformations and ionization occur. However, in a relatively wide range of temperatures ($T < 3000\,K$) and gas-dynamic conditions, characteristic, in particular, for combustion processes, it is sufficient to limit ourselves by consideration of chemical and vibrational nonequilibrium only. The processes of excitation and deactivation of translational and rotational degrees of freedom of molecules occur much faster, and they can be considered completed [2] (see also [19,20,30]), and the processes of ionization of components typical for problems [1–38] at $T < 3000\,K$ as not yet started [2] (see also [15]). The characteristic times of chemical reactions [1,6,7–33] or the characteristic time of gas flow [3–5,32,34–38] are comparable in magnitude with the characteristic times of vibrational relaxation, which leads to mutual influence processes.

In general, to correctly describe the kinetic process, taking into account the mutual influence of chemical reactions and vibrational relaxation, it is necessary to formulate kinetic equations in the form of population balance equations (microscopic or level-by-level description method). This approach is used when solving problems of studying systems with the simplest composition in order to obtain or extrapolate kinetic constants and evaluate the influence of various factors that occur in real conditions (see, for example, [10–14,20,35,36]). In these problems, only a few vibrational modes involved in a chemical reaction are taken into account (as a rule, this is the dissociation of diatomic molecules). In papers [12,14,20,35,36] the subject of the study was the flow of dissociating N_2, and in papers [10,13] — flow of dissociating pure [10] or diluted by Ar [13] O_2. With an increase in the number of components and reactions, the complexity of the problem increases sharply. In papers [39,40] carbon dioxide and 5-component mixture CO_2, CO, O_2, O, C were studied considering more than 8000 different vibrational states.

When modeling and analyzing ignition and combustion processes under actual conditions (various types of reactors or shock waves), one has to deal with systems of complex composition in the presence of a large number of energy exchange processes and chemical reactions. In such problems, it is advisable to formulate kinetic equations within the framework of the hydrodynamic level of description based on appropriate simplifying assumptions (mode approximation) in the form of macroscopic equations for the concentrations of components and average energies of vibrational degrees of freedom (vibrational modes) [3,4, 8,9,16–18,21–24,31–34,41]. The use of a simplified description raises the question of the validity of the simplifications introduced in certain specific cases. Corresponding testing of the mode approximation by comparison with the solution results of problems formulated at the microscopic (state-to-state) level was carried out in papers [9,18,32,33] for cases of dissociation and exchange reactions of diatomic molecules. The results of such comparison indicate the sufficiency of this approximation, provided that the parameters describing the interaction of chemical reactions and vibrational relaxation processes are correctly selected (see also [13,14,37]).

Note that other approaches are aimed at correct consideration of the role of anharmonicity and the shape of the vibrational distribution, as well as at reducing the computational complexity of the problem. In the papers [39,40] a hybrid mode approach for polyatomic gases was formulated, based on averaging the level-by-level rates of vibrational relaxation and chemical reactions, and a comparison of solutions was carried out. Other hybrid approaches combining elements of level-by-level and mode descriptions are proposed in [42,43]. In paper [44] the dissociation calculation was performed taking into account vibrational nonequilibrium based on a new asymptotic method for solving the Boltzmann equation, and the nonequilibrium factor in the dissociation constant is calculated explicitly.

The hydrogen −oxygen system is the simplest (unlike, for example, hydrocarbon oxidation reactions) in terms of the number of components and elementary processes (chemical reactions and energy exchange processes). The importance of this system study from the point of view of fundamental science is that it is a model system containing all the key details of the kinetics of ignition, combustion and detonation processes [45]. After the studies of Semenov and Hinshelwood (1927 — Nobel Prize 1957), the reaction of hydrogen with oxygen was the object of close study. However, the problem of a quantitative description of the kinetics in this system remains unsolved, both from the point of view of agreement between the results of various experiments, and from the point of view of agreement between theoretical models and experiment [16,46,47]. The study of ignition and combustion processes in the hydrogen−oxygen system has important practical significance associated with the use of hydrogen as an effective and environmentally friendly energy carrier [48–52]. All kinetic calculations related to the practical use of hydrogen combustion or to the interpretation of experiments were carried out within the framework of the traditional (formal) description of kinetics, in which kinetic equations relate to the concentrations of components only. This approach radically simplifies the problem, and it is justified on the assumption that there is equilibrium in the degrees of freedom of molecules and radicals. Meanwhile, the characteristic relaxation times of internal states, namely the vibrational relaxation times, depend on the conditions and are comparable or even exceed the characteristic times of fast chemical reactions. Ignoring the influence of vibrational non-equilibrium ultimately leads to various formal kinetic schemes, which, along with elementary (one stage) chemical reactions, include complex overall reactions, the detailed mechanism of which is unknown, and their effective rate constants depend on the conditions (see for more details [17,21]). These circumstances are the main reason for the origin of the term „uncertainty“ in relation to reaction rate constants and mechanisms. For example, in recent papers [51,52] the results of computer simulations of fifteen [51] and five [52] mechanisms of hydrogen combustion in engines are compared with experiment and analyzed. Meanwhile, „problem of the reaction mechanism can be considered completely solved only on the basis of quantitative information about the rate constants of elementary chemical processes“ [53].

The term „simplest“ in relation to the reacting system H_2+O_2 is very conditional, since even in this case one has to deal with a large number of components and elementary processes. However, the use of the mode approximation makes it possible to formulate a fairly general closed vibrationally non-equilibrium model that takes into account the dependence of reaction rate constants on the energy of the internal (vibrational) degrees of freedom of molecules [17,21–24,31,41]. The formulation of kinetic equations in the form of population balance equations in this case simply does not make practical sense due to the lack of the required information about the quantitative characteristics of a very large number of elementary processes.

This paper provides a brief overview of our studies [17,21–24,31] on modeling ignition and combustion processes in the hydrogen−oxygen system at relatively low pressures $p < 4\,\mathrm{atm}$ and temperatures $T < 1500\,\mathrm{K}$, when vibrational non-equilibrium is the most important factor determining the mechanism and rate of the process [21,22]. Vibrational non-equilibrium kinetics is described within the framework of a consistent elementary kinetic approach, the essence of which is as follows. Chemical transformations are described by elementary (one stage) bimolecular reactions. „Formal“ [54] trimolecular reactions involving a third body M, $A+B+M=AB+M$, are described explicitly as a sequence of bimolecular recombination reactions $A+B=AB(v)$, with the formation of a vibrationally excited molecule/radical $AB(v)$, and processes of vibrational (VRT and VV′) relaxation $AB(v)+M=AB(v-1)+M$. In this case, $AB(v)$ during the relaxation process can react with other components of the mixture. The central element of this approach (solving equations for average energies of vibrational modes together with equations for concentrations) is the consistent consideration of the vibrational non-equilibrium of the radical HO_2, which is key in the process of chain branching. The reactions $H+O_2=O+OH$ and $H+O_2+M=HO_2+M$ are replaced by a set of elementary processes of formation, intramolecular energy redistribution among modes, monomolecular decomposition and relaxation of a relatively long-living (see [55–58]) vibrationally excited radical $HO_2(v)$, capable of reacting with other components of the mixture.

In relation to the conditions under consideration, in theoretical estimates of the rate constants of elementary processes the multiquantum transitions can be neglected. The lack of experimental data on the rate constants of energy exchange processes can be supplemented by the results of theoretical estimates based on the use of such molecular models as harmonic oscillators, weakly anharmonic oscillators, as well as their sets in the case of polyatomic molecules [59–63]. To estimate the rate constants of elementary chemical reactions, the results of *ab initio* analysis of potential energy surfaces (PES) of molecular systems of the type H_nO_m in combination with use of various versions of the transition state theory and the results of corresponding dynamic calculations become of utmost importance [16,56–58,64–69].

1. Vibrationally non-equilibrium model

Equations of chemical and vibrational kinetics in the general case of a reacting multicomponent gas mixture within the framework of a macroscopic description, i.e. in the form of equations for the average energies of vibrational modes, ε_k, and concentrations of components, n_i, are published in [4] (see also [34]). Previously, they were used to calculate the flow of chemically and vibrationally non-equilibrium multicomponent gas mixtures through the nozzles of combustion gas-dynamic CO_2-lasers [70–72]. These equations are the corresponding moments of the vibrational state population balance equations (Master Equations), obtained using the following simplifying assumptions [43]: (*a*) chemical reactions do not violate the Maxwell distribution; (*b*) rotational degrees of freedom are in equilibrium with translational ones; (*c*) each type of molecular vibrations (mode) is simulated by a quasi-Boltzmann ensemble of harmonic oscillators.

1.1. Isothermal problem ($T = \mathrm{const}$)

In the isothermal case, at a given gas temperature T, and pressure p, these equations have the following form [21,22].

Equations for molar concentrations per unit mass of gas mixture (n_i):

$$\rho\frac{dn_i}{dt} = \sum_{r=1}^{L_1}(\nu'_{ir} - \nu_{ir})(R_r - R'_r),$$

$$R_r = k_r\prod_{j=1}^{N}(\rho n_j)^{\nu_{jr}}, \quad R'_r = k'_r\prod_{j=1}^{N}(\rho n_j)^{\nu'_{jr}}, \tag{1}$$

where N is the number of components of the mixture, L_1 is the number of reactions, all are considered reversible, ρ is density of the mixture. Stoichiometric coefficients ν_{jr} and ν'_{jr} of j-th chemical component, Y_j, in r-th reaction of the chemical kinetics equations (1) correspond to the following notation of the chemical reaction:

$$(r) \quad \sum_{j=1}^{N}\nu_{jr}Y_j \overset{k_r}{\underset{k'_r}{\longleftrightarrow}} \sum_{j=1}^{N}\nu'_{jr}Y_j.$$

The influence of vibrational non-equilibrium on chemical reactions is manifested through the dependence of the corresponding rate constants, k_r, on the vibrational temperatures of the reagent modes:

$$k_r(T, \{T_k\}) = \kappa_r(T, \{T_k\})k_r^0(T). \tag{2}$$

Here $k_r^0 \equiv k_r(T)$ — rate constant of r-th reaction under the condition of thermal equilibrium. Theoretically, the value k_r^0 can be obtained from dynamic calculations by averaging the corresponding cross-sections over the equilibrium distributions of the reagents or as a result of use of various versions of the transition state theory. The value k_r^0 corresponds to the experimentally obtained value of the rate constant, determined in the limit of high pressures. $\kappa_r(T, \{T_k\})$ — non-equilibrium factor, $\{T_k\}$ — set of vibrational temperatures involved in r-th reaction of molecules (reagents), T_k — effective vibrational temperature as a measure of the average energy of k-th vibrational mode, $T_k = \theta_k/\ln[(1+\varepsilon_k)/\varepsilon_k]$, θ_k — characteristic temperature of k-th vibration (the value of the vibrational quantum of the transition $1 \to 0$).

$$\kappa_r(T, \{T_k\}) \equiv \exp\left[E_r^{(V)}\left(1/T - 1/\sum_i \delta_{ri}T_i\right)\right], \tag{3}$$

where $E_r^{(V)}$ — fraction of activation energy attributable to the vibrational degrees of freedom of the reagent molecules, δ_{ri} — relative efficiency of i-th vibrational mode of reagents with vibrational temperature T_i, $\sum_i \delta_{ri} = 1$; we assume here $\delta_{r1} = \delta_{r2} = \ldots$.

Under the assumptions (*a*) and (*b*) — maintaining equilibrium in translational and rotational degrees of freedom during the reaction — we have:

$$E_r^{(V)} = f\left(E_r^{(A)} - (\xi_r + 4)T/2\right), \quad f(x) = \begin{cases} x, & x > 0 \\ 0, & x \le 0 \end{cases}. \tag{4}$$

Here, from the activation energy $E_r^{(A)}$ (height of the activation barrier), the equilibrium values of the energy of relative translational motion, $E_{\mathrm{trans}} = 2T$ (see [73], formula (3.5)), and rotational energy $E_{\mathrm{rot}} = \xi_r T/2$ of molecules participating in r-th reaction are subtracted, ξ_r — the number of rotational degrees of freedom of the reagents. The height of the activation barrier $E_{r'}^{(A)}$ of the reverse reaction r' determines the total vibrational energy of the products of r-th reaction.

Formula (4) plays an important role in describing the interaction between vibrational relaxation processes and chemical reactions. It is based on the approach [1,74,75] developed for dissociation, introduced in [4] for a multicomponent mixture including exchange reactions, and refined in [16]. According to (3), (4), the height of the activation barrier $E_r^{(A)}$ is the main criterion for the degree of influence of the vibrational excitation of the reagents on the rate constant r of the reaction; the result is more accurate for high activation barrier $E_r^{(A)}$ (when $E_r^{(V)} \gg E_{\text{trans}} + E_{\text{rot}} = 2T + \xi_r T/2$), which corresponds to cases of the greatest influence of vibrational nonequilibrium.

Equations for the average numbers of quanta in vibrational modes k (ε_k):

$$\frac{d\varepsilon_k}{dt} = \sum_q \Delta l_k^{(q)} \sum_{i=1}^{N} \gamma_i k_{ji}^{(q)} (Q_q - Q'_q) + (\rho n_j)^{-1} \times \sum_s (\nu'_{js} - \nu_{js})[(\chi_{sk} - \varepsilon_k)(R_s - R'_s)], \qquad (5)$$

$$Q_q = \prod_m \left[\frac{\varepsilon_m^0(1+\varepsilon_m)}{1+\varepsilon_m^0}\right]^{l_{mq}} \prod_n \left[\frac{\varepsilon_n(1+\varepsilon_n^0)}{\varepsilon_n^0}\right]^{l_{nq}},$$

$$Q'_q = \prod_m (\varepsilon_m)^{l_{mq}} \prod_n (1+\varepsilon_n)^{l_{nq}}.$$

The first term on the right side of the equations of vibrational kinetics (5) describes the change in the average energy (in units θ_k) of k-th vibrational mode (mode k belongs to a molecule of the type j) as a result of interaction with other (molecules of the type i) vibrational modes of the gas mixture. The formula was obtained in [60] by summing the equations for the populations of vibrational levels, multiplied by the level number. The use of the assumptions (b) and (c) and the specific form of transition probabilities for harmonic oscillators made it possible to obtain a closed model with the dependence of the right-hand sides of the equations only on the average energies of the modes. Here $\varepsilon_k^0 = \exp(-\theta_k/T)/[1-\exp(-\theta_k/T)]$ — equilibrium value of ε_k, $\gamma_i = n_i/\sum_i n_i$ — molar fraction of the component i, $k_{ji}^{(q)}$ — rate constant of q-th channel of vibrational relaxation during the interaction of molecules of types j and i,

$$k_{ji}^{(q)} = Z_{ji} P_{ji}^{(q)}(m;n), \qquad (6)$$

Z_{ji} — collision frequency, $P_{ji}^{(q)}(m;n)$ — probability of q-th process of vibrational energy exchange, in which upon collision of molecules of types j and i in modes m there is a decrease in vibrational quantum numbers v_m by l_{mq}, and in modes n — increase in v_n by l_{nq}. When using the model of harmonic oscillators for modes participating in q-th process, the probability of such a process is uniquely characterized by the probability of the corresponding transition between the lowest states

$$P_{ji}\begin{Bmatrix} l_{mq}, & 0 \\ 0, & l_{nq} \end{Bmatrix}.$$

Kinetic quantities of this type characterize the processes of exchange by vibrational energy between modes considered as a whole. In the simplest (most important for the conditions under consideration) case of single-quantum ($l_{mq} = l_{nq} = 1$) vibration-vibrational (VV$'$) exchange between modes m, n and translational (VT) exchange of mode m with an atom or molecule of type i ($l_{mq} = 1$, $l_{nq} = 0$) we have

$$P_{ji}^{(q)} = P_{ji}^{(q)}\begin{Bmatrix} 1, & 0 \\ 0, & 1 \end{Bmatrix} \quad \text{and} \quad P_{ji}^{(q)} = P_{ji}^{(q)}\begin{Bmatrix} 1, & 0 \\ 0, & 0 \end{Bmatrix}.$$

The value $\Delta l_k^{(q)}$ in equation (5) means the change in the number of quanta of k-th mode in q-th (q'-th) process ($\Delta l_k^{(q')} = -\Delta l_k^{(q)}$). For the specific used in practice recording of energy exchange processes and the method for calculating $P_{ji}^{(q)}(m;n)$, see Appendices 1 and 2, respectively. The second term in the right side of the vibrational kinetics equation (5) describes the influence of chemical reactions on the process of vibrational relaxation. Summation over s in (5) is carried out for reactions in which the molecule j with mode k is formed. In the kinetic scheme and in equation (1), the direction of mode formation corresponds to the reaction either r or r'. Here χ_{sk} — the average number of vibrational quanta acquired by k-th mode in one act of formation of molecule of type j (to which mode k belongs) in s-th reaction:

$$\chi_{sk} = E_{s'}^{(V)} \eta_{sk}/\theta_k. \qquad (7)$$

The full set of values η_{sk} characterizes the intermode energy distribution in the products of s-th reaction. Here the value $E_{s'}^{(V)}$, determined by the formula (4), is the fraction of the activation energy of the reverse reaction s' attributable to the vibrational degrees of freedom of the reaction s products (reaction s' reagents). Within the framework of this model it is natural to assume a uniform distribution of energy $E_{s'}^{(V)}$ between the vibrational modes of the products ($\eta_{s1} = \eta_{s2} = \ldots$, $\sum_i \eta_{si} = 1$). The isothermal model serves as a good approximation for interpreting the shock wave experiments on the system H_2+O_2+Ar with small additions of the reacting mixture; see, for example, the results of comparing the calculation [17] with experiment [76] (incident shock wave, stoichiometric mixture 0.93% H_2+0.46% O_2+98.61% Ar). However, when using an isothermal kinetic model, the self-heating of the reacting mixture is completely ignored. This can be the cause of significant errors in calculations even for highly diluted mixtures, when the concentration of the reacting additive is $\leq 5\%$ [31].

1.2. Non-isothermal problem

In relation to shock wave experiments for the reacting gas mixture behind the shock wave under adiabatic conditions, two cases are considered: $V = \text{const}$ (at constant volume, reflected shock wave [47,77–79]); and $p = \text{const}$ (at constant pressure, incident shock wave [76,80]). Under adiabatic conditions of chemical reactions and vibrational relaxation processes, the equations of state and energy conservation should be added to the kinetic equations (1), (5) (see [81] for vibrationally equilibrium mixture and [31]).

Equation of state $p = n_\Sigma \rho R_0 T$, where $n_\Sigma = \sum_{i=1}^{N} n_i$, R_0 — universal gas constant, subject to $V = \text{const}$, $\rho = \rho(t = 0) = \text{const}$, in differential form:

$$d\ln p/dt - d\ln T/dt - d\ln n_\Sigma/dt = 0. \tag{8}$$

Energy conservation equation

$$E(t) = \sum_{i=1}^{N} E_i\big(T(t), t\big) n_i(t) = \text{const}, \tag{9}$$

where E — energy of unit of mass of vibrationally non-equilibrium gas mixture, E_i — non-equilibrium molar energy of i-th component [K/mol], which depends on time t both directly and through temperature T, which changes with time t, being in its turn an independent variable. Under the assumptions (a) and (b) — equilibrium in translational and rotational degrees of freedom — we assume

$$E_i\big(T(t), t\big) = \Delta_f H_i^0 + 3T/2 + \xi_i T/2 + \sum_{k=1}^{N_i} \theta_k \varepsilon_k(t), \tag{10}$$

where N_i — the number of vibrational modes and ξ_i — the number of rotational degrees of freedom in i-th molecule, $\Delta_f H_i^0$ — heat of formation at $T = 0\,\text{K}$. After differentiation (10) (under conditions of adiabaticity and constant volume), equation (9) in differential form looks like

$$C_V \frac{dT}{dt} + \sum_j n_j \sum_{k=1}^{N_j} \theta_k \frac{d\varepsilon_k}{dt} + \sum_i E_i \frac{dn_i}{dt} = 0. \tag{11}$$

Here (and further) i — any component of the mixture (summation over all components), j — vibrationally nonequilibrium component of the mixture, $C_V = \sum_i n_i C_V^{(i)}$ — heat capacity per unit of mass of gas mixture at constant volume for translational and rotational degrees of freedom of molecules, $C_V^{(i)} = (\partial E_i/\partial T)_V$ — molar heat capacity of translational and rotational degrees of freedom of i-th component.

At $p = \text{const} = p(t = 0)$ the equation of state in differential form

$$d\ln n_\Sigma/dt + d\ln\rho/dt + d\ln T/dt = 0. \tag{12}$$

The energy equation is reduced to the enthalpy conservation equation

$$H(t) = \sum_{i=1}^{N} H_i\big(T(t), t\big) n_i(t) = \text{const},$$

or in differential form

$$C_p \frac{dT}{dt} + \sum_j n_j \sum_{k=1}^{N_j} \theta_k \frac{d\varepsilon_k}{dt} + \sum_j H_i \frac{dn_i}{dt} = 0. \tag{13}$$

Here H_i — specific enthalpy of i-th component [K/mol], $H_i = E_i + T$, $C_p = \sum_i C_p^{(i)} n_i$ — heat capacity per unit of mass of the mixture, $C_p^{(i)}$ — molar heat capacity of the i-th component at constant pressure ($C_p^{(i)} = C_V^{(i)} + 1$). For molecules OH^*, O_3, and H_2O_2, considered as equilibrium (see below), $\varepsilon_k = \varepsilon_k(T) = \exp(-\theta_k/T)/[1 - \exp(-\theta_k/T)]$.

Testing of formula (10) (under the condition of thermodynamic equilibrium) by comparison with tabular data for the value $H^0(T) - H^0(0)$ [82] showed that for the conditions under consideration such representation gives an error of about 1% or less.

When numerically solving the system of equations (1), (5), and (8), (11) (or (12), (13)) with respect to n_i, ε_k and p, T (or ρ, T) as initial conditions at $t = 0$ values n_i and ε_k are used, corresponding to the state of the gas mixture before the shock wave front ($T = 300\,\text{K}$). Temperature, pressure and density at the initial moment of time $t = 0$ are taken to be equal to their values behind the shock wave front.

2. Kinetic scheme

The kinetic scheme given below describes vibrationally non-equilibrium kinetics within the framework of consistent elementary kinetic approach and is the result of analysis of papers [16,56–58,64–69] relating the dynamics of atomic-molecular processes taking into account the electronic excitation of atoms O, molecules O_2 and experimentally detected radicals OH. This scheme of chemical reactions and vibrational relaxation channels is the final result of numerous kinetic calculations [17,21,22,24] to identify processes that are most important from the point of view of their influence on experimentally measured values. The kinetic scheme includes the following components: H_2, O_2, H_2O, HO_2, H, O, OH, H_2O_2 and O_3 in the ground electron states, and $O_2(^1\Delta)$, $O(^1D)$ and $OH(^2\Sigma^+)$ (designated as O_2^*, O^* and OH^*). We consider vibrational nonequilibrium of the modes H_2, OH, O_2, O_2^*, $HO_2(100)$, $HO_2(010)$, $HO_2(001)$, $H_2O(100)$, $H_2O(010)$ and $H_2O(001)$ (the later are designated as $HO_2(\nu_1)$, $HO_2(\nu_2)$, $HO_2(\nu_3)$, $H_2O(\nu_1)$, $H_2O(\nu_2)$ and $H_2O(\nu_3)$). The influence of vibrational non-equilibrium of the components OH^*, O_3 and H_2O_2 is neglected due to their low content and rapid relaxation.

Modeling of vibrational non-equilibrium chemical kinetics in the hydrogen−oxygen system was also carried out in [32,33,41], where non-equilibrium of the initial components and OH, preliminary vibrational and electronic excitation of the initial components were considered.

Table 1. The most significant chemical reactions and their equilibrium rate constants $k_r^0 = A_r(T/298.15)^n \times \exp(-E_r^A/T)$ (cm^3, mol, s) in the reacting mixture H_2+O_2+Ar [24,31]

cr	Reactions	M	A_r	n	$E_r^{(A)}$, K
c1	$H_2+O_2=H+HO_2-26.7^a$	–	$4.36\cdot10^{12}$	1.80	25872
c2	$H+O_2=HO_2+25.2$	–	$8.91\cdot10^{13}$	0	0
c3	$HO_2=O+OH-33.8$	–	$1.45\cdot10^{14}$	1.155	33800
c4	$H+O_2=O+OH-8.3$	–	$2.40\cdot10^{11}$	3.00	8360
c5	$H_2+OH=H_2O+H+7.5$	–	$1.60\cdot10^{11}$	1.60	1660
c6	$H_2+O=H+OH-0.96$	–	$7.40\cdot10^{12}$	0.861	4650
c7	$H+HO_2=2OH+17.3$	–	$3.80\cdot10^{13}$	0.486	103
c8	$O+HO_2=OH+O_2+25.7$	–	$2.61\cdot10^{13}$	0.06	650
c9	$2OH=H_2O+O+8.4$	–	$2.07\cdot10^{10}$	2.70	−1251
c10	$2HO_2=H_2O_2+O_2+17.5$	–	$2.77\cdot10^{12}$	0.459	158
c11	$OH+HO_2=H_2O+O_2+34.1$	–	$5.80\cdot10^{13}$	−0.322	112
c12	$H+OH=H_2O+59.6$	–	$4.00\cdot10^{12}$	0.5	400
c13	$2H=H_2+52.0$	–	$7.00\cdot10^{12}$	0.5	300
c14	$2O=O_2+59.6$	–	$6.00\cdot10^{12}$	0.5	300
c15	$O+H=OH+51.0$	–	$6.50\cdot10^{12}$	−0.5	450
c16	$H_2+HO_2=OH+H_2O+24.9$	–	$2.6\cdot10^{11}$	0	1075
c17	$O_3+M=O_2+O+M-11.8$	M^b	$2.98\cdot10^{13}$	−1.15	11830
c18	$O_3+O=2O_2+47.5$	–	$1.34\cdot10^{12}$	0.75	1580
c19	$O_3+H=OH+O_2+39.2$	–	$1.64\cdot10^{13}$	0.75	0
c20	$O_3+H=HO_2+O+13.3$	–	$4.52\cdot10^{11}$	0.75	0
c21	$H_2+HO_2=H_2O_2+H-8.7$	–	$2.56\cdot10^{12}$	0	10750
c22	$H+H_2O_2=OH+H_2O+33.6$	–	$4.64\cdot10^{12}$	0	1760
c23	$H_2O_2+O=HO_2+OH+7.7$	–	$1.00\cdot10^{12}$	2.0	2000
c24	$H_2O_2+OH=HO_2+H_2O+16.1$	–	$1.00\cdot10^{12}$	0	670
c25	$H+HO_2=H_2+O_2^*+15.4$	–	$6.47\cdot10^{11}$	1.67	3160
c26	$O_2^*+M=O_2+M+11.3$	H_2	$1.5\cdot10^{6}$	0.25	0
		O_2	$1.0\cdot10^{6}$	0.25	0
		Ar	$2.94\cdot10^{5}$	−0.25	0
		H_2O	$6.60\cdot10^{6}$	−0.22	0
c27	$O_2^*+H=OH+O+3.0$	–	$7.0\cdot10^{13}$	1.0	7500
c28	$H_2+O^*=H_2O+81.2$	–	$4.00\cdot10^{11}$	−0.5	0
c29	$H+HO_2=H_2O+O^*+3.1$	–	$4.84\cdot10^{13}$	0	892
c30	$O^*+M=O+M+23.0$	M^b	$1.0\cdot10^{11}$	0	0
c31	$H_2+HO_2=OH^*+H_2O-21.9$	–	$1.00\cdot10^{13}$	0	36000
c32	$OH^*+M=OH+M+47.0$	Ar	$1.3\cdot10^{11}$	0.5	0
		H_2O	$1.2\cdot10^{13}$	0.5	0
c33	$OH^*+O_2=HO_2+O+21.1$	–	$1.0\cdot10^{13}$	0.5	0
c34	$OH^*+H_2O=H_2O_2+H+12.7$	–	$7.5\cdot10^{12}$	0	276
c35	$O^*+H_2=OH^*+H-25.4$	–	$8.0\cdot10^{13}$	0	25200
c36	$OH^*+O_2=O_3+H$		$2.0\cdot10^{13}$	0.5	0
c37	$OH^*+M\rightarrow O+H+M-4.0$	H_2	$8.1\cdot10^{13}$	0.45	8060
		OH, H_2O	$5.8\cdot10^{14}$	−0.73	4017
c38	$OH^*+H_2=H_2O+H$	–	$4.0\cdot10^{13}$	0.5	0
c39	$OH^* \rightarrow OH + h\nu$	–	$1.4\cdot10^{6}$	0	0

Note. ^{a} — the thermal effect of reactions is given in 10^3 K; here and below the equal sign means an abbreviated notation for two reactions (direct, r, and reverse, r'); $k_r^0/k_{r'}^0 = K_r$, K_r — equilibrium constant. Reverse reactions (c37′) and (c39′) are not taken into account as unlikely under the conditions under consideration (single arrow), ^{b} — M as an inert particle with concentration $n_\Sigma = \sum_i n_i$.

While the approach is common (see, for example, [9]) of these studies and our studies, there are differences in details, for example, the list of reactions and exchange processes differs primarily with regard to the radical $HO_2(v)$.

2.1. Chemical reactions

The most important reactions that determine the mechanism of chemical transformations and their equilibrium rate constants, k_r^0 (see (2)), are given in Table 1.

The dynamic behavior of the triatomic system H−O−O [54,67–69] is an intermediate case between regular (direct mechanism) and completely chaotic (statistical) behavior („approximation of strong coupling between modes or RRKM approximation " [54]). The latter is modeled at the kinetic level by the following processes: (I) formation of a vibrationally excited radical $HO_2(v)$ as a result of bimolecular recombination and uniform intramolecular redistribution of the $H{-}O_2$ binding energy between HO_2 modes, $H+O_2 \rightarrow HO_2(v)$; (II) dissociation along bond $H{-}O_2$, $HO_2{=}H+O_2$; (III) dissociation along bond $O{-}OH$, $HO_2{=}O+OH$ (reactions (c2) and (c3) in Table 1). In order to take into account at the kinetic level the contribution of regular dynamic behavior (~ 0.1 of the phase space), in addition to the processes (I)−(III) an elementary (single-stage, by direct mechanism) reaction $H+O_2 \rightarrow O+OH$ (reaction (c4) in Table 1) shall be added to the kinematic scheme.

Consistent accounting of vibrational relaxation processes of HO_2, H_2O, H_2, O_2, O_2^* and OH eliminates the need to include in the kinetic scheme formal reactions of the type $A+B+M \rightarrow AB+M$ with an intuitive selection of the efficiencies of third bodies, M; see reactions (c2), (c3′), (c12)−(c15), (c28) in Table 1. On the other hand, ignoring the vibrational non-equilibrium of O_3, H_2O_2 and OH^* determines the inclusion of formal recombination reactions in the calculation in the form $A+B+M \rightarrow AB+M$; reaction (c17) in Table 1 (corresponding reactions for H_2O_2 and OH^* are not given, since their influence is negligible [31]). For the rate constants of trimolecular recombination reactions, k^0_{rec}, the calculations used (recalculated through the equilibrium constant) upper estimates satisfying the relations $k^0_{\mathrm{dis}} < Z_{\mathrm{coll}} \exp(-D/T)$, where Z_{coll} — the maximum possible pre-exponential factor corresponding to the collision frequency, D — dissociation energy [21,22].

Table 1 does not contain the reaction $HO_2+H{=}\ H_2O+O$, which long ago is assumed to be non-elementary [83]. According to *ab initio* analysis of the PES of the system H_2O_2 and dynamic calculations using the classical trajectory method, performed in [16], known in the literature value of the reaction rate constant $HO_2+H{=}H_2O+O$ should be attributed to the reaction (c29), followed by the quenching of atoms O^* in reactions (c28), (c30) and (c35). Reaction (c35) is one of the important reactions of the formation of experimentally detected radicals OH^* [24].

2.2. Vibrational relaxation channels

The channels of collisional vibrational-translational (VT) and vibrational-vibrational (VV′) energy exchange are given in Tables 2 and 3, respectively. Rate constants of VV′ exchange in the representation $k_{ji}^{(q)} = a_{ji}^{(q)} \exp(b_{1ji}^{(q)} T^{-1/3} + b_{2ji}^{(q)} T^{-2/3})$ describe the calculation results with acceptable accuracy (error maximum 10%) (see Appendix 2).

As initial values, theoretical estimates were used (see Appendix 2), based on the use and modernization (in relation to the conditions under consideration) of the theory SSH (Schwartz−Slavsky−Herzfeld) [84] (see also [60]) and the SSHM variant (Schwartz−Slavsky−Herzfeld −Moor) of this theory, which in the simplest way takes into account vibrational-rotational (VR) energy transfer [85–87]. In [88] using the example CO_2 it is shown that the SSH model can give a significant error when calculating the rate of intermode exchanges in a polyatomic gas in comparison with the more accurate model of a forced harmonic oscillator, FHO, developed in [89]. For the considered here VV′ exchange processes the models SSH and SSHM presumably provide sufficient accuracy. The SSH and FHO models do not take into account the influence of rotation on the VT relaxation process; to estimate this effect in [22] data based on the results of papers [90–92] were used.

The VT exchange times (Table 2) and VV′ exchange rate constants (Table 3) were obtained by matching the calculated values τ_{50} (the moment of reaching half of the maximum concentration of the radical OH), τ^* (moment of reaching maximum concentration of OH^*) and τ_{ign} (beginning of luminescence of OH^*) with the corresponding results of measurements [47,76–80] in incident [76,80] and reflected [47,77–79] shock waves. A comparison of the calculated values with the experimentally measured ones shows that of all channels of vibrational relaxation (Tables 2, 3) the VT exchange processes are the most important; they occur with a change in the number of quanta and determine the rate at which equilibrium is established in the system as a whole. In turn, the most important are the relaxation channels of vibrational modes of HO_2 ($q = 5{-}7$), which directly determine the rate of chain branching as a result of the processes $HO_2(v) \rightarrow O+OH$ and $HO_2(v)+M \leftrightarrow HO_2+M$. The quantitative aspect of the kinetics of VV′ exchange processes in the mixture under study mainly comes down to the correct consideration of the fastest (near-resonant) processes that occur without changing the number of vibrational quanta and form the intermediate quasi-stationary state („mixing of quanta" [61]).

As for the kinetics of VT relaxation of vibrational modes of HO_2 ($q = 5{-}7$), then, first of all, it should be noted that this aspect of the behavior of the radical HO_2 was poorly studied from both experimental and theoretical point of view. The SSH and SSHM estimates are based on the assumption of independence of molecular vibrations (modes), i.e., neglecting the disturbances caused by their interaction during a collision. In the case of the radical HO_2 (a nonlinear molecule with an angular deformation vibration), such perturbations are most likely large. Simplifying as much as possible the problem of collision-induced intramolecular intermode interaction when calculating the characteristic VT relaxation times of vibrational modes of HO_2, the molecule is represented as a set of coupled oscillators exchanging energy with the translational and rotational degrees of freedom through the fastest relaxing mode; in this case — this is a low-frequency mode of HO_2; see processes (v5) −(v7) Table 2.

Table 2. VT exchange channels in reacting mixture H_2+O_2+Ar and their characteristic times $p\tau_q^{(M)}=a_q^{(M)}\exp(b_q^{(M)}T^{-1/3})$, s·atm [31]

vq	VT exchange channel	M	$a_q^{(M)}$	$b_q^{(M)}$
v1	$H_2(1)+M=H_2(0)+M$	H_2, OH, H_2O	$1.2 \cdot 10^{-10}$	100
		O_2, O_2^*	$2.4 \cdot 10^{-10}$	101
		Ar	$9.2 \cdot 10^{-10}$	104
v2	$OH(1)+M=OH(0)+M$	H_2	$2.15 \cdot 10^{-7}$	13.9
		OH, H_2O	$3.33 \cdot 10^{-8}$	30.6
		O_2, O_2^*	$1.81 \cdot 10^{-6}$	30.6
		Ar	$2.4 \cdot 10^{-7}$	32.7
v3	$O_2(1)+M=O_2(0)+M$	H_2, OH, H_2O	$1.89 \cdot 10^{-9}$	49.5
		O_2, O_2^*	$1.0 \cdot 10^{-10}$	138
		Ar	$5.0 \cdot 10^{-11}$	173
v4	$O_2^*(1)+M=O_2^*(0)+M$	H_2	$1.03 \cdot 10^{-9}$	48.0
		OH, H_2O	$1.07 \cdot 10^{-9}$	48.0
		O_2, O_2^*	$1.1 \cdot 10^{-10}$	134
		Ar	$5.6 \cdot 10^{-11}$	169
v5	$HO_2(001)+M=HO_2(000)+M^a$	H_2	$5.6 \cdot 10^{-12}$	97
v6	$HO_2(010)+M=HO_2(000)+M$	O_2, O_2^*	$6.00 \cdot 10^{-10}$	96.34
v7	$HO_2(100)+M=HO_2(000)+M$	H_2O, OH	$1.00 \cdot 10^{-12}$	98.43
		Ar	$1.20 \cdot 10^{-7}$	53.00
v8	$H_2O(100)+M=H_2O(000)+M$	H_2	$1.56 \cdot 10^{-8}$	79.6
v9	$H_2O(001)+M=H_2O(000)+M$	OH, H_2O	$2.43 \cdot 10^{-8}$	74.1
		O_2, O_2^*	$5.17 \cdot 10^{-8}$	74.1
		Ar	$1.50 \cdot 10^{-8}$	81.3
v10	$H_2O(010)+M=H_2O(000)+M$	H_2	$1.41 \cdot 10^{-9}$	89.1
		OH, H_2O	$9.07 \cdot 10^{-6}$	−4.47
		O_2, O_2^*	$1.93 \cdot 10^{-5}$	−4.47
		Ar	$1.29 \cdot 10^{-10}$	122

Note. ^{a} — similar for (v5)−(v7).

3. Comparison of calculation with experiment

This Section is based on papers [17,21,22,31].

Direct study of the chemical processes kinetics under actual conditions of their occurrence in nature or in engineering (for example, during combustion or detonation) is complicated by side factors of diffusion, convection, heat release and heat transfer, which are superimposed on the main chemical process and in some cases can play a decisive role. This leads to the appearance in theoretical models of a large number of parameters (in addition to kinetic characteristics), often either unknown or having a high degree of uncertainty, which greatly complicates the quantitative interpretation of experiments, introducing uncertainty into model kinetic schemes.

The shock tube method was long ago used as a method for experimentally studying the kinetics of hydrogen oxidation (see, for example, the review [93]). Experimental results obtained by this method are especially convenient for comparison with kinetic calculations. The history of experimental studies of the hydrogen-oxygen reaction in shock waves covers more than half a century, however, in published articles, as a rule, there is not enough information to compare the measurement results with calculations. Rare exceptions are papers [47,76–80], which provide the values of temperature and pressure (but not only the pressure range) at which measurements were made. This is especially important when using vibrational non-equilibrium model due to the direct dependence of the rates of vibrational relaxation of molecules and radicals on pressure.

Table 4 lists the systems H_2+O_2+Ar, which were studied experimentally by the shock tube method in papers [76,80] (incident wave) and [47,77–79] (reflected wave). The results were compared with the corresponding results of kinetic calculations within the framework of vibrationally non-equilibrium model using a unified kinetic scheme (Table 1−3).

Characterizing in general the results of comparison of experimental data [47,76–80] for the system H_2+O_2+Ar at temperatures $T < 1500$ K and pressures $p < 4$ atm, we state the qualitative and quantitative agreement of the calculation results [17,22,31] with the experimental data. In the

Table 3. VV′ exchange channels and their rate constants in representation $k_{ji}^{(q)} = a_{ji}^{(q)} \exp(b_{1ji}^{(q)} T^{-1/3} + b_{2ji}^{(q)} T^{-2/3})$, s^{-1}, in reacting mixture H_2+O_2+Ar[21,22]

vq	VV′ exchange channel	$a^{(q)}$	$b_1^{(q)}$	$b_2^{(q)}$	Note
v11	$H_2(1)+H_2O(000)\leftrightarrow H_2(0)+H_2O(001)$	$1.50 \cdot 10^5$	32.53	−160.6	[a]
v12	$H_2(1)+HO_2(000)\leftrightarrow H_2(0)+HO_2(100)$	$9.50 \cdot 10^4$	31.71	−171.1	[a]
v13	$H_2(1)+H_2O(000)\leftrightarrow H_2(0)+H_2O(100)$	$1.55 \cdot 10^5$	31.32	−175.5	[a]
v14	$H_2(1)+OH(0)\leftrightarrow H_2(0)+OH(1)$	$1.13 \cdot 10^5$	30.07	−187.5	[a]
v15	$H_2(1)+O_2(0)\leftrightarrow H_2(0)+O_2(1)$	$2.22 \cdot 10^5$	14.17	−273.1	[b]
v16	$H_2(1)+H_2O(000)\leftrightarrow H_2(0)+H_2O(010)$	$1.53 \cdot 10^4$	14.64	−271.0	[b]
v17	$H_2(1)+O_2^*(0)\leftrightarrow H_2(0)+O_2^*(1)$	$2.50 \cdot 10^5$	13.60	−275.5	[b]
v18	$HO_2(100)+H_2O(000)\leftrightarrow HO_2(000)+H_2O(100)$	$4.31 \cdot 10^5$	34.85	−105.2	[a]
v19	$HO_2(100)+OH(0)\leftrightarrow HO_2(000)+OH(1)$	$5.66 \cdot 10^4$	32.61	−159.5	[a]
v20	$HO_2(100)+O_2(0)\leftrightarrow HO_2(000)+O_2(1)$	$1.36 \cdot 10^5$	−0.5415	−335.9	[b]
v21	$HO_2(100)+O_2^*(0)\leftrightarrow HO_2(000)+O_2^*(1)$	$1.54 \cdot 10^5$	−1.676	−341.0	[b]
v22	$OH(1)+H_2O(000)\leftrightarrow OH(0)+H_2O(010)$	$1.04 \cdot 10^4$	13.93	−274.0	[b]
v23	$OH(1)+O_2(0)\leftrightarrow OH(0)+O_2(1)$	$1.39 \cdot 10^5$	13.42	−276.2	[b]
v24	$OH(1)+O_2^*(0)\leftrightarrow OH(0)+O_2^*(1)$	$1.58 \cdot 10^5$	12.55	−279.9	[b]
v25	$OH(1)+HO_2(000)\leftrightarrow OH(0)+HO_2(010)$	$1.22 \cdot 10^3$	11.34	−285.0	[b]
v26	$O_2(1)+O_2^*(0)\leftrightarrow O_2(0)+O_2^*(1)$	$1.01 \cdot 10^5$	34.41	−118.2	[a]
v27	$O_2(1)+HO_2(000)\leftrightarrow O_2(0)+HO_2(010)$	$7.79 \cdot 10^2$	32.93	−154.5	[a]
v28	$O_2^*(1)+HO_2(000)\leftrightarrow O_2^*(0)+HO_2(010)$	$8.40 \cdot 10^2$	34.02	−131.3	[a]
v29	$HO_2(010)+HO_2(000)\leftrightarrow HO_2(000)+HO_2(001)$	$6.56 \cdot 10^2$	34.00	−131.9	[b]
v30	$H_2O(001)+HO_2(000)\leftrightarrow H_2O(000)+HO_2(100)$	$4.32 \cdot 10^5$	34.37	−119.6	[a]
v31	$H_2O(001)+H_2O(000)\leftrightarrow H_2O(000)+H_2O(100)$	$1.27 \cdot 10^5$	33.84	−136.3	[a]
v32	$H_2O(001)+OH(0)\leftrightarrow H_2O(000)+OH(1)$	$1.01 \cdot 10^5$	32.46	−161.6	[a]
v33	$H_2O(001)+HO_2(000)\leftrightarrow H_2O(000)+HO_2(011)$	$6.23 \cdot 10^2$	24.64	−224.2	[b]
v34	$H_2O(001)+H_2O(000)\leftrightarrow H_2O(000)+H_2O(010)$	$1.49 \cdot 10^4$	9.955	−290.8	[b]
v35	$H_2O(001)+O_2(0)\leftrightarrow H_2O(000)+O_2(1)$	$2.05 \cdot 10^5$	9.428	−293.0	[b]
v36	$H_2O(001)+O_2^*(0)\leftrightarrow H_2O(000)+O_2^*(1)$	$2.30 \cdot 10^5$	8.534	−296.7	[b]
v37	$H_2O(001)+HO_2(000)\leftrightarrow H_2O(000)+HO_2(010)$	$1.05 \cdot 10^4$	7.296	−301.9	[b]
v38	$H_2O(100)+OH(0)\leftrightarrow H_2O(000)+OH(1)$	$9.71 \cdot 10^4$	34.15	−127.4	[a]
v39	$H_2O(100)+HO_2(000)\leftrightarrow H_2O(000)+HO_2(011)$	$6.08 \cdot 10^2$	25.63	−218.6	[b]
v40	$H_2O(100)+H_2O(000)\leftrightarrow H_2O(000)+H_2O(010)$	$1.47 \cdot 10^4$	10.65	−287.8	[b]
v41	$H_2O(100)+O_2(0)\leftrightarrow H_2O(000)+O_2(1)$	$2.02 \cdot 10^5$	10.11	−290.1	[b]
v42	$H_2O(100)+O_2^*(0)\leftrightarrow H_2O(000)+O_2^*(1)$	$2.27 \cdot 10^5$	9.192	−293.9	[b]
v43	$H_2O(100)+HO_2(000)\leftrightarrow H_2O(000)+HO_2(010)$	$1.04 \cdot 10^4$	7.919	−299.3	[b]
v44	$H_2O(010)+O_2(0)\leftrightarrow H_2O(000)+O_2(1)$	$7.17 \cdot 10^3$	34.69	−108.6	[a]
v45	$H_2O(010)+O_2^*(0)\leftrightarrow H_2O(000)+O_2^*(1)$	$7.93 \cdot 10^3$	34.19	−125.9	[a]
v46	$H_2O(010)+HO_2(000)\leftrightarrow H_2O(000)+HO_2(010)$	$3.63 \cdot 10^2$	33.03	−152.9	[a]
v47	$H_2O(010)+HO_2(000)\leftrightarrow H_2O(000)+HO_2(001)$	$6.30 \cdot 10^3$	33.26	−149.0	[b]

Note. [a] — SSH evaluation.[b] — SSHM evaluation. See Appendix 2.

absolute majority of cases (for more details, see [31]), the values τ_{50} and τ^* are reproduced in calculations almost exactly (the difference is maximum 5%). Some difference between the measured and calculated values τ_{ign} ($\approx$ 10%), apparently, is a consequence of differences in the determination of this vaues in the papers [78] and [31] (see Note c in Table 4).

3.1. Characteristic relaxation time of the radical HO_2

When matching the calculated values τ^*, τ_{50} and τ_{ign} with the values obtained experimentally, the main thing was the variation and selection of essentially unknown kinetic constants characterizing the processes of vibrational-translational and vibrational-vibrational exchange involving modes of HO_2 [21,22,31]. For the compositions and conditions under consideration at $T < 1500$ K, the most important processes turned out to be VT energy exchange of modes of HO_2 (the key role of the radical $HO_2(v)$ in the hydrogen oxidation reaction). During the final matching of the calculated values τ^*, τ_{50} and τ_{ign} and the experimentally measured values, the only variable parameter was $\tau_5^{(H_2)}$, i.e. characteristic time of V−RT energy exchange, identical (Table 2) for all three modes of the radical HO_2 during its collisions with molecules H_2. The average value of $\tau_5^{(H_2)}$ (given in Table 2) should

Table 4. Systems H_2+O_2+Ar, studied experimentally [47,76-80], the results of which were compared with the corresponding results of kinetic calculations [17,22,31]. Φ — fuel excess coefficient

System, Experiment	Composition			Φ	Measured values	Calculation, problem
	% H_2	% O_2	% Ar			
I, [76] IW[a]	0.93	0.46	98.61	1.0	τ^{*c}	[17,22], T = const
II, [80] IW	2.0	1.0	97.0	1.0	τ^*	[22], T = const
III, [80] IW	4.0	1.0	95.0	2.0	τ^*	[22], T = const
IV, [77] RW[b]	2.0	0.5	97.5	2.0	$\tau_{50}{}^d$	[17,22], T = const
III, [77] RW	4.0	1.0	95.0	2.0	τ_{50}	[31], V = const
IV, [77] RW	2.0	0.5	97.5	2.0	τ_{50}	[31], V = const
V, [78] RW	3.0	1.5	95.5	1.0	τ^*, $\tau_{\text{ign}}{}^e$	[31], V = const
VI, [78] RW	1.03	0.5	98.47	1.03	τ^*, τ_{ign}	[31], V = const
VII, [78] RW	3.36	1.14	95.5	1.47	τ^*, τ_{ign}	[31], V = const
VIII, [79] RW	1.69	0.81	97.5	1.04	τ_{ign}	[31], V = const
IV, [79] RW	2.0	0.5	97.5	2.0	τ_{ign}	[31], V = const
IX, [47] RW	1.5	1.5	97.0	0.5	τ^*, τ_{50}	[31], V = const

Note. [a] — incident wave (IW), [b] — reflected wave (RW), [c] — time between passage of shock front ($t = 0$) and the moment of maximum radiation at a wavelength ≈ 306 nm (in calculation — the moment of reaching maximum concentration of OH*), [d] — time between passage of shock front and the moment when the absorption of light by OH radical reached half of its maximum value (in the calculation the moment of reaching half the maximum concentration of OH radical), [e] — time between passage of shock front and the moment of radiation start (in our calculations it was assumed that τ_{ign} is approximately equal to achievement of 0.01 of maximum concentration of OH*).

be considered as a quantitative estimate of the currently unknown value of $\tau^{(H_2)}_{HO_2}$. The maximum deviation from the average value was 1.5 times (in both directions) at $T \approx 1000$ K [22], processing of new experimental data led to a scatter by 2.5 times at $T \approx 1300$ K [31]. This error characterizes our ignorance of the details of the dynamics of elementary reactions expressed at the kinetic level by the variables $E_r^{(V)}$, δ_{rk} and η_{rk}, as well as the influence of other approximations used; see relations (3), (4), (7) and (10).

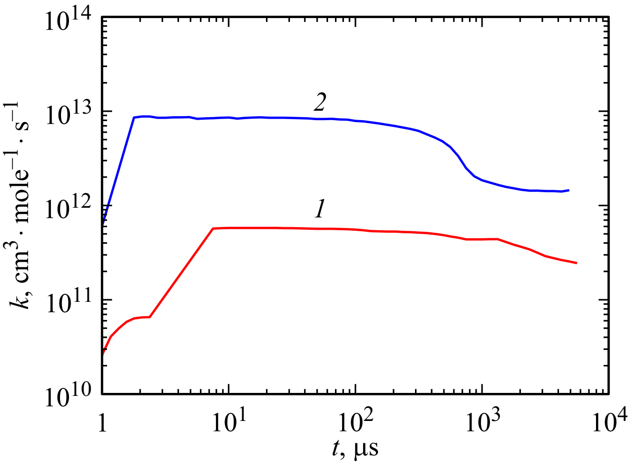

Figure 1. Time dependences of the value $k^{\text{eff}}_{H+O_2 \to O+OH} = R_3/[H][O_2]$ (effective rate constant of the overall process $H+O_2 \to O+OH$) for two calculation options [17]: *1* — system I, $T = 1050$ K, $p = 1.9$ atm, experiment [76]; *2* — system III, $T = 1052$ K, $p = 2.2$ atm, experiment [77].

3.2. Dependence of the effective chain branching constant on experimental conditions

In contrast to the traditional equilibrium description of kinetics, which can not provide a quantitative interpretation of various experiments without varying the reaction rate constants, taking into account vibrational non-equilibrium solves the problem of consistency of the theoretical model with experimental results obtained by different authors using different methods for different compositions and conditions. It is the non-equilibrium (in terms of vibrational degrees of freedom) nature of the process that is the reason for the observed dependence on experimental conditions of the effective rate constant of the overall reaction $H+O_2 \to O+OH$ [17], activation energy of which varies within $6790 \leq E^A \leq 11430$ K according to estimates in various experiments [46]. In the mechanism of chemical transformations adopted here, such reaction is absent. The rate of the chain branching process is mainly determined by the rate R_3 of the monomolecular decomposition of a vibrationally excited radical HO_2 —

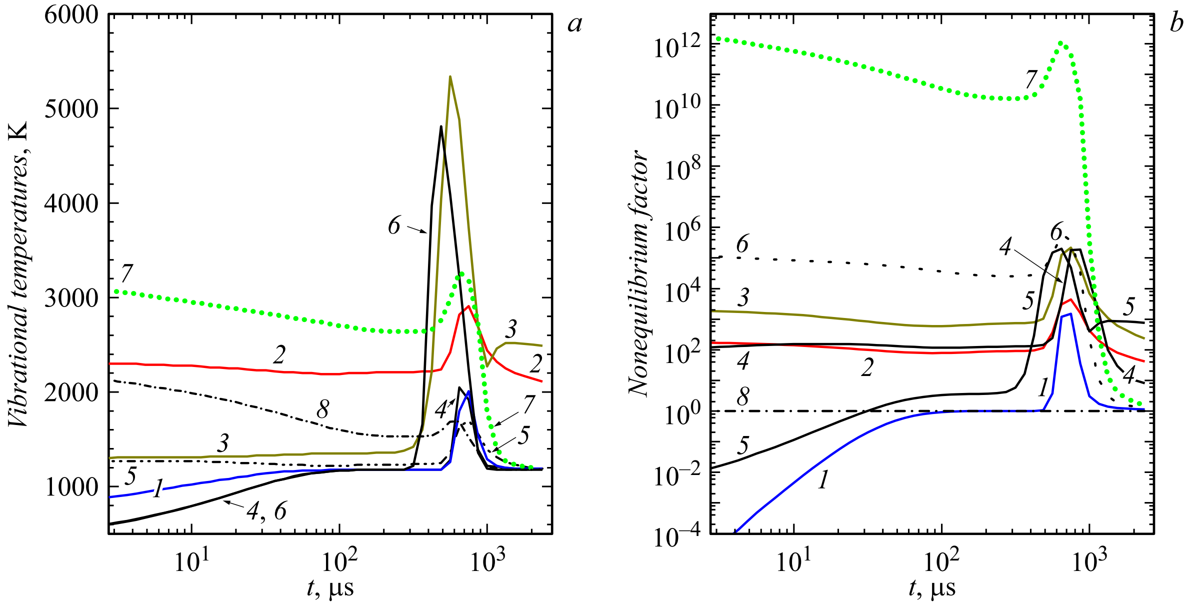

Figure 2. Time dependences of vibrational temperatures T_k (a) and non-equilibrium factors κ_r (b). $T = 1178,\mathrm{K}$; $p = 1.675\,\mathrm{atm}$ (system I, calculation [22]). Curves (a) correspond to the vibrational temperatures of the following modes: 1 — H_2, 2 — $HO_2(\nu_1)$, 3 — OH, 4 — O_2, 5 — $HO_2(\nu_3)$, 6 — O_2^*, 7 — $H_2O(\nu_1)$ and 8 — $H_2O(\nu_2)$. Curves (b) correspond to the non-equilibrium factors of the following reactions (Table 1): 1 — (c1), 2 — (c2′), 3 — (c3), 4 — (c31), 5 — (c8′), 6 — (c11 ′), 7 — (c12′), 8 — reactions (c1′), (c2), (c3′), (c31′), (c8), (c11), (c12).

by reaction (c3) Table 1. The effective rate constant of the overall process $H+O_2 \rightarrow O+OH$ is extracted from the calculation as $k^{\mathrm{eff}}_{H+O_2\rightarrow O+OH} = R_3/[H][O_2]$. The influence of experimental conditions is illustrated in Fig. 1, which shows the values $k^{\mathrm{eff}}_{H+O_2\rightarrow O+OH}$ depending on time, obtained in calculations corresponding to experiments [76] (stoichiometric mixture, registration of OH^* radiation) and [77] (rich mixture, registration of OH absorption) for almost identical temperatures $T = 1050$ and $1052\,\mathrm{K}$, respectively (Table 4).

The pronounced dependence on pressure and time of the effective rate constant of the most important overall reaction, which determines the rate of the entire process as a whole, is a consequence of the non-equilibrium nature of its occurrence and the changing role of various elementary reactions and vibrational relaxation channels at various stages of the process.

4. Vibrational non-equilibrium and thermal effect at various stages of the reaction

This Section is based on papers [21,22,31].

The non-equilibrium by the vibrational degrees of freedom nature of the reaction in the mixture H_2+O_2+Ar behind the shock wave is illustrated in Fig. 2, which shows typical time dependences of vibrational temperatures, T_k, and non-equilibrium factors, $\kappa_r(T, \{T_k\})$ [21,22]. The difference between the rate constants and their equilibrium values can be orders of magnitude, i.e., in the conditions under consideration the nature of this reaction is non-equilibrium, and the vibrational non-equilibrium of the radical HO_2 is the most significant feature of the hydrogen oxidation process.

Fig. 3 shows the thermal effects, Q, and the corresponding temperatures of the translational and rotational degrees of freedom of molecules (gas temperatures), T, for two calculation options [31] with almost identical temperatures behind the shock wave front. The calculations simulate experiments for the following two typical systems: IV, $T = 1174\,\mathrm{K}$, $p = 0.945\,\mathrm{atm}$, registration of the radical OH by absorption [77]; and V, $T = 1173\,\mathrm{K}$, $p = 1.3\,\mathrm{atm}$, registration of the radical OH^* by radiation [78].

The vibrationally non-equilibrium nature of the reaction of hydrogen with oxygen behind the shock wave front manifests itself throughout the entire process. At the initial stage, vibrational excitation of the initial molecules H_2 and O_2 occurs from the initial (room) temperature at $t = 0$ to the equilibrium gas temperature, T, behind the shock wave front (Fig. 2). At this stage, the process of hydrogen oxidation proceeds as endothermic; the main reactions are the initiation reaction (c1) and the elementary non-statistical process (c4), significant at times $t \leq 1\,\mu\mathrm{s}$.

At the stage of intense reaction, the most important contribution to the heat release and, consequently, to the increase in gas temperature is made by fast reactions (c2),

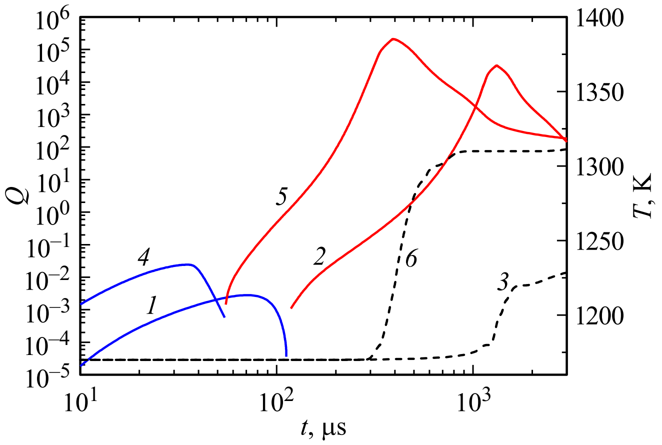

Figure 3. Positive, Q^+ (heat release, curves *2, 5*), negative, Q^- (heat absorption, curves *1, 4*) thermal effects and gas temperatures, T (curves *3, 6*), for the next two calculation options [31]: system IV, $T = 1174\,\mathrm{K}$, $p = 0.945\,\mathrm{atm}$ (curves *1–3*) and system V, $T = 1173\,\mathrm{K}$, $p = 1.3\,\mathrm{atm}$ (curves *4–6*).

(c5), (c7), (c9), (c11), (c13), (c1′). In the reactions (c1′), (c7), (c11), (c2), (c13) (and other bimolecular recombination reactions), energy is released partially in the form of energy of translational and rotational degrees of freedom of molecules. In reactions (c5) and (c9), energy is released predominantly in the form of energy in the translational and rotational degrees of freedom of the product molecules. Just these reactions are responsible for the explosive nature of self-heating of the reacting mixture during the combustion and detonation of hydrogen.

The calculation options illustrated in Fig. 3 (systems IV and V at practically identical temperatures and relatively close pressures behind the shock wave front) differ significantly in composition. In this case, we have for ΔT (temperature change as a result of self-heating of the reacting mixture) 53 K (system IV) and 147 K (system V). As calculations shown [31], ΔT unambiguously correlates with the value of the stoichiometric part of the mixture (SPM); so, ΔT decreases from $\approx 150\,\mathrm{K}$ at SPM = 4.5% to $\approx 50\,\mathrm{K}$ at SPM = 1.5%. For compositions with SPM < 1.5% the kinetic calculations performed within the framework of the isothermal formulation of the problem can serve as a satisfactory approximation.

5. Mechanism of formation of electronically excited radical OH($^2\Sigma^+$)

This Section is based on papers [22,24].

Emission of electronically excited radical $\mathrm{OH}^*(^2\Sigma^+)$,

$$\mathrm{OH}^*(^2\Sigma^+) \to \mathrm{OH}(\mathrm{X}^2\Pi) + h\nu, \quad h\nu \cong 47\,000\,\mathrm{K}\ (\lambda \approx 306\,\mathrm{nm}),$$

is long ago used in research practice to determine the time of ignition induction in this system [93–96]. In experiments, where the shock tube method is used, the end of the induction period is associated with the moment of maximum emission of the radical OH*, which is a very informative quantity, responding even to minor changes in the parameters of the gas mixture in temperature, pressure and composition, and can be measured with high accuracy. In a formal (equilibrium) description of the kinetics, the mechanism of formation of the radical OH* is postulated as a set of reactions reverse to the bimolecular quenching reactions of OH* in collisions with molecules and radicals of the reacting mixture $\mathrm{H_2{+}O_2}$+inert diluent. Such processes, in particular, include the trimolecular recombination processes $\mathrm{H{+}O^*{+}M{\rightarrow}OH^*{+}M}$ and the reverse predissociation process $\mathrm{H{+}O{+}M{\rightarrow}OH^*{+}M}$ [76].

As for the elementary processes of quenching of the electronically excited radical OH*, a significant number of experimental and theoretical studies [16,76,97–101] are devoted to the study of the kinetics and dynamics of these processes.

Considering the mechanism of formation of the electronically excited radical OH* at the elementary kinetic level at relatively low pressures ($p < 10\,\mathrm{atm}$), it should be borne in mind that the triple collisions of H+O+M and $\mathrm{H{+}O^*(^1D){+}M}$ can obviously be neglected due to their low probability. For example, the trimolecular reaction $\mathrm{H{+}O_2{+}H_2{=}OH^*{+}H_2O}$, proposed even in [94] and explaining the formation of electronically excited radical OH* at the earliest stages of the combustion process, within the framework of vibrationally non-equilibrium model is considered [17,21,22] as occurring in two stages ($\mathrm{H{+}O_2 \rightarrow HO_2(v)}$ and $\mathrm{HO_2(v){+}H_2 \rightarrow OH^*{+}H_2O}$) through the formation of a vibrationally excited radical $\mathrm{HO_2(v)}$, reactions (c2) and (c31) Table 1.

Reactions involving the electronically excited radical OH* and their equilibrium rate constants, k_r^0 (see (2)), are given in Table 1. The values are taken from papers [21,22] and are the final result of comparison of measured [76,80] values τ^* (moment of maximum emission at wavelength 306.4 nm) with the corresponding calculated values (moment of maximum concentration of OH*), obtained in [21,22] using the unified kinetic scheme. The input data for these rate constants were experimental results [97,98], estimates by the transition state method based on *ab initio* analysis of potential energy surfaces (PES) [16,17,76], as well as the results of dynamic calculations [99,100].

Main reactions (c1)–(c3), (c5)–(c7), (c12) provide a chain mechanism of ignition and combustion of hydrogen, and, together with the characteristic relaxation time of the radical $\mathrm{HO_2}$, determine the value τ^*. The total rates of reactions of formation of OH* are 4–5 orders of magnitude lower than the rates of these basic reactions [22,24]. Reactions involving OH* do not affect the rate of ignition and combustion of hydrogen in general.

The most important (Table 1) in terms of their contribution to the overall process of formation of the radical OH*

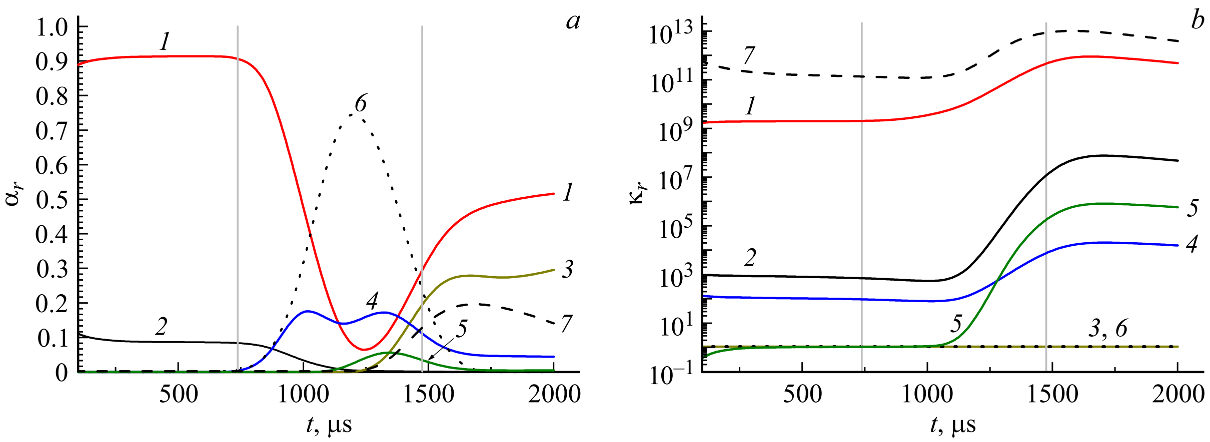

Figure 4. Time dependences of relative contributions, α_r (*a*), into the total rate of reactions of OH^* formation and the corresponding non-equilibrium factors, κ_r (*b*); system II, $T = 1060$ K, $p = 0.64$ atm. The curve numbers in the Figures (*a*) and (*b*) correspond to the following reactions in Table 1: *1* — (c32 ′), *2* — (c31), *3* — (c36′), *4* — (c33′), *5* — (c35), *6* —(c34′), *7* — (c38′). Vertical light gray lines indicate the values τ^* and $\tau^*/2$.

are the following reactions:

$$\text{(c31)}\ H_2(v) + HO_2(v) \rightarrow OH^* + H_2O$$

(at the initial stage of the process),

$$\text{(c32}', \text{ M=Ar)}\ OH(v) + Ar \rightarrow OH^* + Ar,$$

$$\text{(c36}'\text{)}\ O_3 + H \rightarrow OH^* + O_2,$$

$$\text{(c34}'\text{)}\ H_2O_2 + H \rightarrow OH^* + H_2O,$$

$$\text{(c38}'\text{)}\ H_2O(v) + H \rightarrow OH^* + H_2,$$

$$\text{(c33}'\text{)}\ HO_2(v) + O \rightarrow OH^* + O_2,$$

$$\text{(c35)}\ O^* + H_2(v) \rightarrow OH^* + H.$$

Just these reactions, changing roles in terms of relative contribution, α_r, depending on the conditions relating composition, temperature and pressure, determine the mechanism of formation of the radical OH^* (Fig 4, *a*).

Figure 4, *b* shows the values of the non-equilibrium factor, κ_r, corresponding to the reactions (c31), (c32′, M=Ar), (c36′), (c34′), (c38′), (c33′) and (c35) (see formulas (2)−(4)). The values $\kappa_r \gg 1$ (curves *1, 2, 4, 5, 7* in Fig. 4, *b*) indicate to the fact that the corresponding reactions (c32′, M=Ar), (c31), (c33′), (c35) and (c38′) proceed in non-equilibrium mode with respect to vibrational degrees of freedom, overcoming high activation barriers (46 990, 36 000, 21 150, 25 200 and 54 400 K, respectively) due to vibrational excitation of the reagents. So, for example, in the case illustrated in Fig. 2, superequilibrium excitation — the ratio of the average energy to its equilibrium value, $\varepsilon_k(t)/\varepsilon_k^0(T)$ — for vibrational modes H_2, $HO_2(\nu_1)$, OH and $H_2O(\nu_1)$ reaches values of 8.68, 17.3, 47.5 and 21.6, respectively (curves *1, 2, 3, 7* Fig. 2, *b*). These energies correspond to vibrational temperatures: $T_{H_2} = 2010$, $T_{HO_2(\nu_1)} = 2910$, $T_{OH} = 5340$ and $T_{H_2O(\nu_1)} = 3270$ K.

For reactions (c36′) and (c34′) (curves *3, 6* in Fig. 4, *b*) the values $\kappa_r = 1$ (equilibrium mode) are the consequence of the simplifying assumption (we neglect the influence of vibrational non-equilibrium of O_3, and H_2O_2), originally laid down in the formulation of the kinetic scheme [21]. This approximation, which is applicable (as calculations have shown) in the case of rich and stoichiometric mixtures ($\Phi \geq 1$), may turn out to be insufficient for quantitative description of the kinetics in the case of lean mixtures ($\Phi < 1$).

Regarding the processes of quenching the radical OH^*, we note the following. The total contribution of these processes is close in magnitude to the total contribution of the OH^* formation processes, differing from the latter in value in maximum the second digit. The most important reactions of quenching the radical OH^* (in order of importance) are the following reactions: (c38), (c36) at the initial stage, (c32, M=H_2O), (c39), (c34) and (c37, M=H_2O).

6. Inhibition of reaction of hydrogen with oxygen by additions of polyatomic gases

This section is based on paper [23].

The inhibiting effect of polyatomic gas additives on the reaction of hydrogen with oxygen was discovered in the middle of the last century and was observed experimentally using a number of hydrocarbons (from pentane to octane), as well as low alcohols, methane and propane [102]. In subsequent decades, due to the extreme practical importance of the problem of inhibiting the gas-phase combustion, explosion and detonation, ethane [103,104], formaldehyde [105], ethylene [106] and other polyatomic gases, including halogen-substituted (fully or partially) hydrocarbons [107–109] were added to this list. In the cited

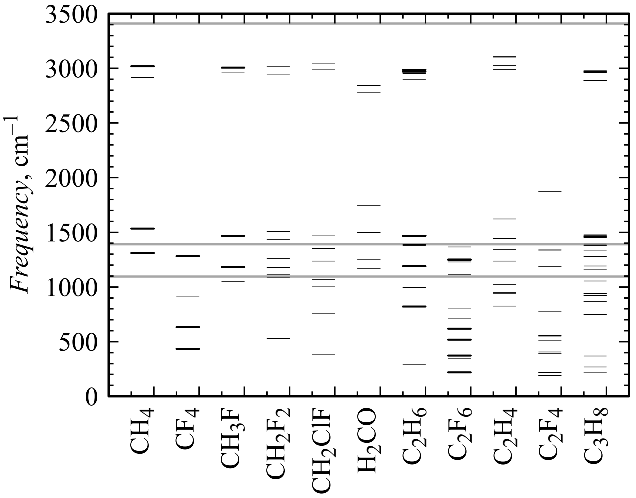

Figure 5. Fundamental vibrational frequencies (ground electronic state frequencies) of some hydrocarbons, halogenated hydrocarbons and formaldehyde compared with the fundamental vibrational frequencies of the radical HO_2 (solid light gray lines). Bold lines indicate doubly degenerate or closely spaced non-degenerate vibrational states of inhibitor compounds.

papers the inhibition mechanism is associated exclusively with the chemical activity of inhibitors or their combustion products, leading to the recombination of chain carriers such as H, O and OH, the most important of which in stoichiometric and rich mixtures is H atom[102,103,107]. When studying the effect of the additive CF_2Cl_2 on the ignition of hydrogen and methane, the vibrationally excited molecules HF ($v = 2$, 3) [109] were identified, which may indicate a chemical vibrationally non-equilibrium process of inhibition.

In the paper [23] the effect of inhibition of the reaction of hydrogen with oxygen by additives of polyatomic gases was studied by numerical modeling of the process within the framework of the vibrationally non-equilibrium model. It is shown that the effect can be explained by the inhibitor influence on the rate of vibrational relaxation of the radical $HO_2(v)$ formed during the reaction in vibrationally excited state.

Figure 5 [23] shows, against the background of the main vibrational frequencies of the radical HO_2 ($\nu_1 = 3410\,cm^{-1}$, $\nu_2 = 1390\,cm^{-1}$ and $\nu_3 = 1095\,cm^{-1}$), the main vibrational frequencies of methane (CH_4), tetrafluoromethane (CF_4), fluoromethane (CH_3F), difluoromethane (CH_2F_2), chlorofluoromethane (CH_2ClF), formaldehyde (H2CO), ethane (C_2H_6), hexafluoroethane (C_2F_6), ethylene (C_2H_4), tetrafluoroethylene (C_2F_4) and propane (C_3H_8). In general, the choice of specific substances from among the known inhibitors was arbitrary. Further, to denote polyatomic inhibiting additive instead of a chemical formula, we will often use the general designation inh. It can be seen that the highest frequencies of normal vibrations of many molecules are relatively close to the vibrational frequency ν_1 of the radical HO_2: the corresponding frequency ratios are $\nu_1^{\mathrm{inh}}/\nu_1 \approx 0.9$. As for the lower vibrational frequencies of inhibitor molecules, almost each of them has frequencies close to ν_2 and/or ν_3 of the radical HO_2, and therefore the corresponding frequency ratios are equal to or approximately equal to unity. All this indicates the presence of at least one high-speed resonant or near-resonant channel of VV′ exchange of inhibitor with $HO_2(v)$. The behavior of the energy received inhibitor can naturally be characterized by fast processes of energy redistribution between modes and VT relaxation through the mode with the lowest frequency.

To take into account the most important in terms of speed processes of VV′ and VT energy exchange in the reacting system H_2+O_2+inh, keeping simple the problem, the inhibitor molecule is considered as a multimode oscillator having four vibrational frequencies ν_1^i, ν_2^i, ν_3^i and ν_4^i. The first three of these frequencies are closest to frequencies ν_1, ν_2, and ν_3 of the radical HO_2, respectively. The value ν_4^i corresponds to the minimum vibrational frequency of the inhibitor to take into account VT energy exchange process of the inhibitor molecule with the molecules and atoms of the gas mixture. Thus, the kinetic scheme describing the process of initiation and chain branching in the system H_2+O_2+inh$+$Ar (Table 3) shall, at a minimum, be supplemented with the following vibrational relaxation channels:

$$(\mathrm{vi1})\,\mathrm{HO_2}(100) + \mathrm{inh}_{k=1}(0) \to \mathrm{HO_2}(000) + \mathrm{inh}_{k=1}(1),$$

$$(\mathrm{vi2})\,\mathrm{HO_2}(010) + \mathrm{inh}_{k=2}(0) \to \mathrm{HO_2}(000) + \mathrm{inh}_{k=2}(1),$$

$$(\mathrm{vi3})\,\mathrm{HO_2}(001) + \mathrm{inh}_{k=3}(0) \to \mathrm{HO_2}(000) + \mathrm{inh}_{k=3}(1),$$

$$(\mathrm{vi4–vi7})\,\mathrm{inh}_k(1) + \mathrm{M} \to \mathrm{inh}_k(0) + \mathrm{M},\ k = 1, 2, 3, 4, \ldots.$$

Here channels (vi1)−(vi3) describe the processes of single-quantum VV′ energy exchange of vibrational modes of the inhibitor (frequencies ν_1^i, ν_2^i and ν_3^i), with the corresponding vibrational modes of the radical HO_2 (frequencies ν_1, ν_2 and ν_3), and the channels (vi4, vi5, . . .) describe the processes of VT relaxation of the inhibitor through the mode with the lowest frequency ν_4^i under the assumption of rapid energy redistribution between modes.

The key parameter that determines the value of the rate constant of q-th vibrational-vibrational energy exchange $k_{\mathrm{VV'}}^{(q)}$ between two modes of colliding molecules is the ratio of their frequencies (see Appendix 2). In [23] for the rate constants of processes (vi1) −(vi3) the minimum values of their dependences on the corresponding frequency ratios ν_k^i/ν_k (closest in magnitude to ν_k) were used as bottom estimate (Fig. 6).

In paper [23] to estimate the characteristic times of inhibitor VT relaxation in the reacting mixture H_2+O_2+inh$+$Ar at $T = 1140\,K$ experimental data [112–114] obtained at $T \approx 300\,K$ were used. The extrapolation was carried out under the assumption that the Landau−Teller dependence is valid for τ_{VT}, which can quite reasonably be attributed to the temperature range considered here (see, for example, Chapter IV in [2]):

$$\tau_{\mathrm{VT}} = [Z_{10}(1 - \exp(-\theta/T))]^{-1} = a\exp(bT^{-1/3}),$$

Table 5. Results of calculation of the minimum concentration of the additive γ_{inh} (upper estimate), inhibiting the combustion of hydrogen in a mixture of $4\%\mathrm{H}_2{-}1\%\mathrm{O}_2{-}(95{-}\gamma_{\mathrm{inh}})$ %Ar after incident shock wave at $T = 1142$ K and $p = 0.71$ atm

Inh	ν_4^i, cm^{-1}	τ_{VT}, s	Frequencies ratio in VV′ exchange process			Rate constants of VV′ exchange $^{b)}$, s^{-1}			γ_{inh}, vol.%
			vi1	vi2	vi3	vi1	vi2	vi3	
CH_4	1311	$5 \cdot 10^{-7}$	0.89	0.91	0.84	$2 \cdot 10^5$	$2 \cdot 10^5$	$7 \cdot 10^4$	2.5
CF_4	435	$5 \cdot 10^{-8}$	0.92	0.92	0.83	$2 \cdot 10^5$	$2 \cdot 10^5$	$6 \cdot 10^4$	5.7
CH_3F	1049	$1 \cdot 10^{-7}$	0.88	0.95	0.96	$1 \cdot 10^5$	$7 \cdot 10^5$	$8 \cdot 10^5$	1.9
CH_2F_2	528	$2 \cdot 10^{-8\,a)}$	0.88	0.91	1.00	$1.5 \cdot 10^5$	$2 \cdot 10^5$	$1 \cdot 10^7$	0.4
CH_2ClF	554	$2 \cdot 10^{-8\,a)}$	0.89	0.94	0.98	$2 \cdot 10^5$	$3.5 \cdot 10^5$	$2 \cdot 10^6$	1.3
H_2CO	1167	$1 \cdot 10^{-5\,a)}$	0.83	0.90	0.94	$67 \cdot 10^4$	$1.7 \cdot 10^5$	$3.5 \cdot 10^5$	4.6
C_2H_6	289	$1.1 \cdot 10^{-8}$	0.88	1.00	0.91	$1.3 \cdot 10^5$	$1 \cdot 10^7$	$2 \cdot 10^5$	0.32
C_2F_6	125	$1.25 \cdot 10^{-8\,a)}$	0.40	0.98	0.98	$1.5 \cdot 10^3$	$2 \cdot 10^6$	$2 \cdot 10^6$	0.79
C_2H_4	826	$3 \cdot 10^{-8\,a)}$	0.91	0.97	0.93	$2 \cdot 10^5$	$1 \cdot 10^6$	$3 \cdot 10^5$	0.14
C_2F_4	190	$1.25 \cdot 10^{-8\,a)}$	0.55	0.96	0.92	$4 \cdot 10^3$	$5 \cdot 10^5$	$2 \cdot 10^5$	0.7
C_3H_8	216	$1.3 \cdot 10^{-8}$ [113]	0.87	1.00	0.96	$1 \cdot 10^5$	$1 \cdot 10^7$	$5 \cdot 10^5$	0.31

Note.,^{a} — upper estimate by formula $\tau_{\mathrm{VT}} = \tau_c Z_{10}$ ($\tau_c = 5 \cdot 10^{-10}$ s, Z_{10} see. Fig. 6), b — bottom estimate by values of rate constants and the number of considered VV′ exchange processes.

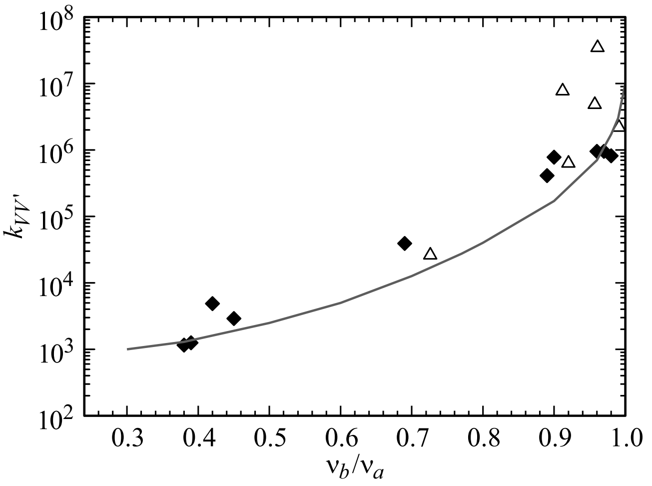

Figure 6. Dependence of rate constant of vibrational-vibrational VV′ exchange at 1140 K on the ratio of frequencies of energy exchanging vibrational modes a and b of interacting molecules. Points marked with black diamonds refer to system H–O [21,22], by light triangles — to system C–N–O [110,111]. Solid line — values, accepted in calculations as lower estimate of $k_{\mathrm{vv}'}$.

$$Z_{10} = ZP_{10},$$

where Z_{10} — the number of collisions leading to the excitation/deactivation of vibrations, Z — the total number of molecule collisions per unit of time ($Z = 1/\tau_c$), τ_c — average time between collisions. Fig. 7 shows the experimentally measured values Z_{10} for a number of polyatomic molecules depending on the lowest vibrational frequency [112]. The effect of inhibiting the reaction of hydrogen with oxygen by additions of polyatomic gases is demonstrated in [23] using a specific example of system III (Table 4) at $T = 1142$ K, $p = 0.71$ atm, which

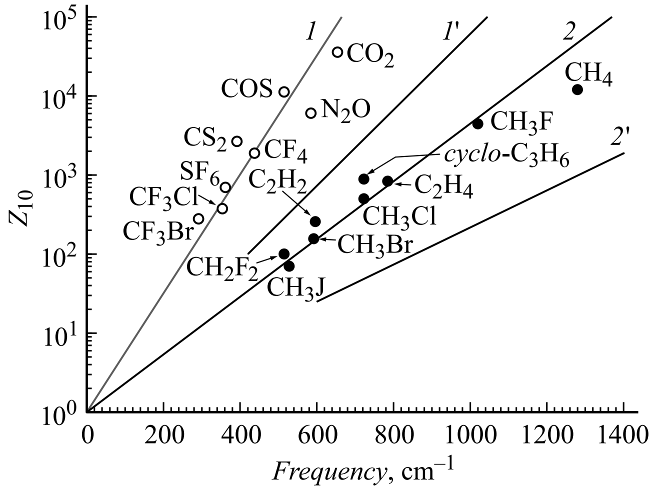

Figure 7. [23]. Dependences Z_{10} on the lowest vibrational frequency of polyatomic molecules at temperature of 300 K (light dots on the straight line *1*, black dots on the straight line *2*) [112]. Straight lines *1′* and *2′* are obtained from straight lines *1* and *2*, respectively, by recalculating to temperature of 1140 K using the relation $\tau_{\mathrm{VT}} = Z_{\mathrm{VT}} \tau_c$ at $\tau_c = 5 \cdot 10^{-10}$ s (upper estimate). In the case of low vibrational frequencies ($\nu_4^i < 600$ cm^{-1}), $Z_{10} = 10^2$ was taken as upper estimate.

was experimentally studied in the paper [80]. In the absence of the inhibitor the observed chemical reaction is a consequence of the vibrationally non-equilibrium nature of the process (see, for example, Fig. 2). At times $700-800\,\mu$s ($t = 0$ — the moment of passage of the shock wave front) at the stage of intensive reaction, the maximum rates of consumption H_2, O_2 and formation H_2O are achieved, maximum concentrations of intermediates are observed, including the radical OH^* detected by its emission (in this case $\tau^* = 820\,\mu$s). The non-equilibrium rate constant of the most important process of chain branching (c3) $HO_2 \rightarrow O + OH$ exceeds its equilibrium value by 5 orders of magnitude ($\kappa_{c3} \approx 10^5$ at $t = 800\,\mu$s) (see relation (3)). The inhibitor presence suppresses the reaction, which stops at times $t \approx 600\,\mu$s as a result of accelerating the relaxation of the vibrational modes of the radical HO_2 due to its interaction with the inhibitor through channels of VV′ exchange (vi1) −(vi3) and fast VT relaxation of the inhibitor along channels (vi4), (vi5).

Table 5 shows the results of calculations [23] of the minimum concentration, γ_{inh}, of additives inhibiting the process of hydrogen combustion in a mixture of $4\%\,H_2+1\%\,O_2 + (95-\gamma_{\text{inh}})\%\,Ar$ behind the incident shock wave ($T = 1142\,K$, $p = 0.71$ atm) until it is suppressed. By the value γ_{inh} one can judge the comparative effectiveness of a particular inhibitor. The most effective inhibitors (CH_2F_2, C_2H_6, C_2H_4, and C_3H_8 with $\gamma_{\text{inh}} < 0.5\%$) are those whose molecules are characterized by frequencies close to the corresponding frequencies ν_1, ν_2 and ν_3 of the radical HO_2, and the minimum frequency $\nu_4^i \leq 800\,\text{cm}^{-1}$ ($\tau_{\text{VT}} \approx 10^{-8}$ s) (Fig. 5). Also note that there is a general tendency towards an increase in the effectiveness of a particular inhibitor as the number of its constituent atoms and, consequently, the number of vibrational degrees of freedom increase. The latter increases the probability of resonant and near-resonant VV′ exchange processes of type (vi1)−(vi3) and, naturally, is consistent with experimental data concerning the range of polyatomic molecules known as inhibitors (see publications [102–109] and links therein). The Table also reflects the experimental fact noted in the paper [103] that „ethylene itself is a more effective inhibitor than ethane“.

The paper [23] did not take into account the possible parallel influence of chemical reactions of inhibitor molecules with hydrogen atoms, which proceed, like the reaction (c2) with $k_{\text{I}} \approx 8 \cdot 10^{13}\,\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, practically without activation barrier. Thus, in the paper [107] in the case of hydrogen combustion inhibition by propylene, the reaction $H+C_3H_6 \rightarrow C_3H_7$ with $k \approx 4 \cdot 10^{13}\,\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ was considered as such reaction. Note that the radical C_3H_7 formed in this reaction can also be an equally effective inhibitor precisely as a deactivator of the vibrationally excited radical HO_2(v). Calculation of the parallel contribution of processes of this kind, leading to the recombination of chain carriers, primarily H atoms, requires special attention as a subject for future studies.

Conclusion

The equations of chemical and vibrational kinetics for the average energies of vibrational modes and concentrations of components are applicable in the general case of reacting multicomponent gas mixture. A general scheme for replacing complex reactions with a set of elementary ones is considered. The details of its application determine both the computational difficulty of the problem and the adequacy of the physical picture.

For a mixture of hydrogen−oxygen−inert gas (argon), a diagram of chemical reactions and vibrational relaxation channels is presented, which is the final result of numerous kinetic calculations. The central element of the model is the consistent consideration of the vibrational non-equilibrium of the radical HO_2. This intermediate product is formed in a highly excited vibrational state and further participates in chain branching reactions and the formation of electronically excited particles.

The calculation is compared with experiment using the shock tube method for direct and reflected waves in combination with emission and absorption spectroscopy. For the system H_2+O_2+Ar at temperatures $T < 1500\,K$ and pressures $p < 4$ atm we state the qualitative and quantitative agreement between the results of calculations and experiments using unified kinetic scheme. The selected range is characterized by high sensitivity to reaction parameters and a strong influence of vibrational non-equilibrium. This is illustrated by typical time dependences of vibrational temperatures and non-equilibrium factors. For the effective rate „constant“ of the overall reaction $H+O_2=O+OH$ the estimate was obtained that explains its observed dependence on experimental conditions.

Using vibrationally non-equilibrium model of hydrogen oxidation, the following is shown. Under the above conditions for T and p, the decisive contribution to the total process of OH^* formation is made by reactions occurring in the vibrationally non-equilibrium mode, their activation barrier is overcome due to the vibrational excitation of the reagents. The effect of inhibiting the reaction of hydrogen with oxygen by additives of various polyatomic gases may be associated with their influence on the rate of vibrational relaxation of the radical HO_2(v), but not only with the chemical activity of the inhibitor.

Appendix 1: Specific types of collisional energy exchange

$$\frac{d\varepsilon_k}{dt} = \sum_q \left(\frac{d\varepsilon_k}{dt}\right)^{(q)}_{\text{vibr}} + \left(\frac{d\varepsilon_k}{dt}\right)_{\text{chem}}.$$

Changes in average energies, $(d\varepsilon_k/dt)_{\text{vibr}}$, of k-th vibrational mode as a result of the action of q-th channel of vibrational relaxation, in general form represented by equations (5), in specific cases have the following forms.

Single-quantum VT energy exchange (Table 2, $q = 1-10$):

$$Y_j(1) + Y_i \overset{k_{ji}^{(q)}}{\longleftrightarrow} Y_j(0) + Y_i,$$

mode k belongs to a molecule of the type j, a molecule of the type i does not change its vibrational state, i.e. $l_{mq} = 1$, $l_{nq} = 0$, $\Delta I_k^{(1)} = 1$

$$Q_q = \varepsilon_k^0(1+\varepsilon_k)/(1+\varepsilon_k^0), \quad Q'_q = \varepsilon_k,$$

$$\left(\frac{d\varepsilon_k}{dt}\right)^{(q)}_{\text{vibr}} = \sum_i \gamma_i k_{ji}^{(q)} \frac{\varepsilon_k^0 - \varepsilon_k}{1+\varepsilon_k^0}, \tag{A1.1}$$

$$k_{ji}^{(q)} = (1+\varepsilon_k^0)/\tau_q^{(\mathrm{M})}, \text{ here } \mathrm{M} \equiv Y_i.$$

Single-quantum VV′ energy exchange (Table 3, $q = 11-32$, 34–38, 40–47):

$$Y_j(1) + Y_i(0) \overset{k_{ji}^{(q)}}{\longleftrightarrow} Y_j(0) + Y_i(1),$$

mode k belongs to a molecule of type j, mode l belongs to a molecule of type i, i.e. $l_{mq} \equiv l_{kq} = 1$, $l_{nq} \equiv l_{lq} = l$, $\Delta l_k^{(q)} = 1$, $\Delta l_l^{(q)} = -1$,

$$Q_q = \frac{\varepsilon_k^0(1+\varepsilon_k)}{1+\varepsilon_k^0}\,\frac{\varepsilon_l(1+\varepsilon_l^0)}{\varepsilon_l^0}, \quad Q'_q = \varepsilon_k(1+\varepsilon_l);$$

$$\left(\frac{d\varepsilon_k}{dt}\right)^{(q)}_{\text{vibr}} = \sum_i \gamma_i k_{ji}^{(q)} \left[\frac{\varepsilon_k^0(1+\varepsilon_l^0)}{(1+\varepsilon_k^0)\varepsilon_l^0}(1+\varepsilon_k)\varepsilon_l - \varepsilon_k(1+\varepsilon_l)\right]. \tag{A1.2}$$

$1 \to 2$ quantum VV′ energy exchange (Table 3, $q = 33,\ 39$):

$$Y_j(1) + Y_i(00) \overset{k_{ji}^{(q)}}{\longleftrightarrow} Y_j(0) + Y_i(11),$$

mode k belongs to a molecule of the type j, modes l and p belong to a molecule of the type i, i.e. $l_{mq} \equiv l_{kq} = 1$, $l_{nq} \equiv (l_{lq}, l_{pq}) = (1,\ 1)$, $\Delta l_k^{(q)} = 1$, $\Delta l_l^{(q)} = -1$, $\Delta l_p^{(q)} = -1$,

$$Q_q = \frac{\varepsilon_k^0(1+\varepsilon_k)}{1+\varepsilon_k^0}\,\frac{\varepsilon_l(1+\varepsilon_l^0)}{\varepsilon_l^0}\,\frac{\varepsilon_p(1+\varepsilon_p^0)}{\varepsilon_p^0},$$

$$Q'_q = \varepsilon_k(1+\varepsilon_l)(1+\varepsilon_p);$$

$$\left(\frac{d\varepsilon_k}{dt}\right)^{(q)}_{\text{vibr}} = \sum_i \gamma_i k_{ji}^{(q)} \left[\frac{\varepsilon_k^0(1+\varepsilon_l^0)(1+\varepsilon_p^0)}{(1+\varepsilon_k^0)\varepsilon_l^0\varepsilon_p^0}(1+\varepsilon_k)\varepsilon_l\varepsilon_p - \varepsilon_k(1+\varepsilon_l)(1+\varepsilon_p)\right]. \tag{A1.3}$$

Appendix 2: To calculation of rate constants of vibrational relaxation processes

According to SSH theory [84] (see also [60,61,63]), the probabilities per collision of q-th transition of vibrational energy from modes m to modes n during the interaction of molecules of j-th and i-th types are calculated by the formula:

$$P_{ji}^{(q)}(m;n) \equiv P_{ji}\left\{\begin{matrix} l_{mq}, & 0 \\ 0, & l_{nq} \end{matrix}\right\} = \xi_{ji}^{(q)} \prod_m V_{l_{mq}0}^2 \prod_n V_{l_{nq}0}^2 \times \Phi[\xi_0^{(m)}(1-\omega_n/\omega_m)]. \tag{A2.1}$$

Here $\xi_{ji}^{(q)}$ — orientation factor (varies from 0.1 to 0.02 based on simple considerations of collision dynamics); $V_{l_{mq},0}$ — transition matrix element $0 \to l_{mq}$ of a harmonic oscillator (mode) of the type m participating in q-th process; ω_m — oscillator frequency; $\xi_0^{(m)} = \tau_* \omega_m$ — adiabaticity parameter (Messy parameter averaged over collisions), τ_* — characteristic interaction time; $\Phi(x)$ — adiabaticity factor, taking into account the change in translational energy during exchange with vibrations,

$$\Phi(x) = x^2 \int_0^\infty e^{-z}\,\mathrm{sh}^{-2}(x/\sqrt{z})\,dz$$

$$\cong \begin{cases} 8\sqrt{\pi/3}\,x^{7/3}\exp(-3x^{2/3}), & x \gg 1\ [115], \\ \frac{1}{2}\left[3-\exp\left(-\frac{2}{3}x\right)\right]\exp\left(-\frac{2}{3}x\right), & 0 \le x \le 20\ [116]. \end{cases} \tag{A2.2}$$

Although the dependence (A2.1), (A2.2) was obtained as a result of solving a linear dynamic problem (semiclassical calculation in the first order of perturbation theory for the oscillator model with a driving force) using the exponential repulsion potential, it can be approximately considered universal for many colliding pairs, since rotation and long-range attraction effects can be taken into account by adapting the oscillator parameters ξ_{ji} and ξ_0.

Adiabaticity parameter

$$\xi_0^{(m)} = \pi\beta_m\alpha^{-1}(D_m/kT)^{-1/2}(M_{ji}/\mu_m)^{-1/2}, \tag{A2.3}$$

and matrix elements

$$|V_{10}^{(m)}|^2 \cong \frac{1}{2}\left(\frac{\beta_m}{\alpha}\right)^2, \quad |V_{20}^{(m)}|^2 \cong \frac{1}{8}\left(\frac{\beta_m}{\alpha}\right)^4,$$

$$|V_{30}^{(m)}|^2 \cong \frac{1}{48}\left(\frac{\beta_m}{\alpha}\right)^6 \tag{A2.4}$$

are determined by relations known in the theory of vibrational relaxation (see, for example, [63] and references there). Here, M_{ji} — reduced mass of $j-i$ collision, μ_m — oscillator reduced mass, α — parameter of the intermolecular interaction potential (here we assume

$1/\alpha = 0.2\cdot10^{-8}\,\mathrm{cm}$), D_m and β_m — parameters of the intramolecular potential (corresponding to the Morse potential).

When applying formulas (A2.1) −(A2.4) to the molecule HO_2, the latter was considered as a set of the following harmonic oscillators: the stretching along the bond $H\cdots O$, $HO_2(100)$, with reduced mass 1.0693 and frequency $3698\,\mathrm{cm}^{-1}$; angular vibration relative to the equilibrium value of the angle $\angle HOO = 104.3^\circ$, $HO_2(010)$, with reduced mass of 1.1311 and frequency of $1430\,\mathrm{cm}^{-1}$; the stretching along the bond $O\cdots O$, $HO_2(001)$, with reduced mass of 13.0737 and fundamental frequency of $1120\,\mathrm{cm}^{-1}$.

For processes VT and non-resonant VV′ energy transfer involving molecules that are asymmetrical due to the presence of H atom, the relative translational motion is slow compared to the rotational motion. In the simplest theory of VR energy exchange [85] the dynamic parameters, velocity and reduced mass, characterizing translational motion, are replaced by the corresponding parameters characterizing rotational motion. In this approach the role of translational motion is simply to bring molecules closer together. Consequently, when calculating the rate constants of these processes using the relations (A2.1−A2.4) as an estimate of SSHM instead of (A2.3), we have the following relation (see also [86]):

$$\xi_0^{(m)} \approx \pi\beta\alpha^{-1}(D_m/kT)^{-1/2}. \qquad \text{(A2.5)}$$

The main (Tables 2, 3) VT and VV relaxation channels in the reacting mixture H_2+O_2+Ar at $T \geq 1000\,\mathrm{K}$, $p \sim 1\,\mathrm{atm}$ were selected as a result of a comparative analysis of the values of rate constants calculated for these conditions. This selection was based on the following assessments:

$$[\Phi(x)]_{\min} \sim 2\cdot10^{-4}, \quad \left|V_{10}^{(m)}\right|^2 \sim 0.05,$$

$$\left|V_{20}^{(m)}\right|^2 \sim 10^{-3}, \quad \left|V_{30}^{(m)}\right|^2 \sim 2\cdot10^{-5}, \qquad \text{(A2.6)}$$

i.e. Tables 2, 3 include the processes with the following probability

$$P_{ji}^{(q)} > [\Phi(x)]_{\min}\left|V_{10}^{(m)}\right|^2 = 10^{-5}. \qquad \text{(A2.7)}$$

Of the non-single-quantum transitions, only the processes of VV′ transfer (v33), $H_2O(001)+HO_2(000)\leftrightarrow H_2O(000)+HO_2(011)$, and (v39) $H_2O(100)+HO_2(\ 000)\leftrightarrow H_2O(000)+HO_2(011)$ (Table 3) meet the condition (A2.7).

Funding

This work was performed in accordance with the Russian state tasks AAAA-A19-119071190017-7 and AAAA-A19-119022690098-3.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] P.V. Marrone, C.E. Treanor. Phys. Fluids, **6**, 1215 (1963). DOI: 10.1063/1.1706888

[2] E.V. Stupochenko, S.A. Losev, A.I. Osipov. *Relaksatsionnye protsessy v udarnykh volnakh* (Nauka, M., 1965) (in Russian)

[3] S.A. Losev. *Gazodinamicheskie lazery* (Nauka, M., 1977 (in Russian)

[4] V.M. Vasil'ev, S.V. Kulikov, O.V. Skrebkov. PMTF, **4**, 13 (1977). (in Russian).

[5] K. Smith, R. Thomson. *Chislennoe modelirovanie gazovykh lazerov* (Mir, M., 1981) (in Russian)

[6] A.S. Bashkin, V.I. Igoshin, A.N. Oraevsky, V.A. Shcheglov. *Khimicheskie lazery* (Nauka, M., 1982) (in Russian)

[7] R.C. Brown. Combustion and Flame, **62**, 1 (1985). DOI: 10.1016/0010-2180(85)90088-4

[8] C. Park. *Nonequilibrium Hypersonic Aerothermodynamics* (Wiley, NY., 1990), Document ID 19910029860

[9] O. Knab, H-H. Frühauf, E.W. Messerschmid. J. Thermophys. Heat Transf., **9**, 219 (1995). DOI: 10.2514/3.649

[10] F. Lordet, J.G. Meolans, A. Chauvin, R. Brun. Shock Waves, **4**, 299 (1995). DOI: 10.1007/BF01413872

[11] E.M. Fisher. Combustion and Flame, **108**, 127 (1997). DOI: 10.1016/0010-2180(85)90088-4

[12] E.V. Kustova, E.A. Nagnibeda. Chem. Phys., **233**, 57 (1998). DOI: 10.1016/S0301-0104(98)00092-5

[13] Y. Sakamura. Shock Waves, **13**, 361 (2003). DOI: 10.1007/s00193-003-0176-3

[14] M. Lino da Silva, V. Guerra, J. Loureiro. Chem. Phys., **342**, 275 (2007). DOI: 10.1016/j.chemphys.2007.10.010

[15] M.A. Gallis, R.B. Bond, J.R. Torczynski. J. Chem. Phys., **131**, 124311 (2009). DOI: 10.1063/1.3241133

[16] O.V. Skrebkov, S.P. Karkach. Kinetics and Catalysis, **48** (3), 367 (2007). DOI: 10.1134/S0023158407030044

[17] O.V. Skrebkov, S.P. Karkach, A.N. Ivanova, S.S. Kostenko. Kinetics and Catalysis, **50** (4), 461 (2009). DOI: 10.1134/S0023158409040016

[18] I.V. Arsentiev, B.I. Loukhovitski, A.M. Starik. Chem. Phys., **398**, 73 (2012). DOI: 10.1016/j.chemphys.2011.06.011

[19] M. Lino da Silva, J. Loureiro, V. Guerra. Chem. Phys., **398**, 96 (2012). DOI: 10.1016/j.chemphys.2011.08.014

[20] J.G. Kim, I.D. Boyd. Chem. Phys., **415**, 237 (2013). DOI: 10.1016/j.chemphys.2013.01.027

[21] O.V. Skrebkov. J. Modern Phys., **5**, 1806 (2014). DOI: 10.4236/jmp.2014.516178

[22] O.V. Skrebkov. Combustion Theory and Modeling, **19**, 131 (2015). DOI: 10.1080/13647830.2014.977352

[23] O.V. Skrebkov, S.S. Kostenko. Kinetics and Catalysis, **58** (1), 1 (2017). DOI: 10.1134/S0023158417010098

[24] O.V. Skrebkov, A.L. Smirnov. Kinetics and Catalysis, **59** (5), 545 (2018). DOI: 10.1134/S0023158418050117

[25] C. Lin, A. Xu, G. Zhang, Y. Li. Combustion and Flame, **164**, 137 (2016). DOI: 10.1016/j.combustflame.2015.11.010

[26] C.M. Tarver. J. Phys. Chem. A, **101**, 4845 (1997). DOI: 10.1021/jp9626430

[27] L. Shi, H. Shen, P. Zhang, D. Zhang, C. Wen. Combust. Sci. Technol., **189** (5), 841 (2017). DOI: 10.1080/00102 202.2016.12605 61

[28] K.C. Uy, L. Shi, C. Wen. Combustion and Flame, **196**, 174 (2018). DOI: 10.1016/j.combustflame.2018.06.015

[29] C. Lin, K.H. Luo. Combustion and Flame, **198**, 356 (2018). DOI: 10.1016/j.combustflame.2018.09.027

[30] S.N. Dhurandhar, A. Bansal. Phys. Fluids, **30**, 117104 (2018). DOI: 10.1063/1.5054194

[31] O.V. Skrebkov, S.S. Kostenko, A.L. Smirnov. Int. J. Hydrogen Energy, **45**, 3251 (2020). DOI: 10.1016/j.ijhydene.2019.11.168

[32] A.M. Starik, N.S. Titova. ZhTF, **71** (8), 1 (2001). (in Russian).

[33] I.N. Kadochnikov, I.V. Arsentiev. Shock Waves, **30**, 491 (2020). DOI: 10.1007/s00193-020-00961-0

[34] O.V. Skrebkov, S.V. Kulikov. Chem. Phys., **227**, 349 (1998). DOI: 10.1016/S0301-0104(97)00296-6

[35] M. Capitelli, G. Colonna, F. Esposito. J. Phys. Chem. A, **108**, 8930 (2004). DOI: 10.1021/jp048847v

[36] A. Guy, A. Bourdon, M-Y. Perrin. Chem. Phys., **420**, 15 (2013). DOI: 10.1016/j.chemphys.2013.04.018

[37] S. Voelkel, V. Raman, P.L. Varghese. Shock. Waves, **26**, 539 (2016). DOI: 10.1007/s00193-016-0645-0

[38] A. Zidane, R. Haoui, M. Sellam, Z. Bouyahiaoui. Int. J. Hydrogen Energy, **44**, 4361 (2019). DOI: 10.1016/j.ijhydene.2018.12.149

[39] O. Kunova, A. Kosareva, E. Kustova, E. Nagnibeda. Phys. Rev. Fluids, **5**, 123401 (2020). DOI: 10.1103/physrevfluids.5.123401.

[40] A. Kosareva, O. Kunova, E. Kustova, E. Nagnibeda. Phys. Fluids, **34**, 026105 (2022). DOI: 10.1063/5.0079664.

[41] N.G. Dautov, A.M. Starik. Combustion, Explosion, and Shock Waves, **30** (5), 571 (1994). DOI: 10.1007/BF00755819

[42] I.N. Kadochnikov, I.V. Arsentiev, B.I. Loukhovitski, A.S. Sharipov. Chem. Phys., **562**, 111669 (2022). DOI: 10.1016/j.chemphys.2022.111669.

[43] O.V. Skrebkov. Russ. J. Phys. Chem. B, **5** (2), 227 (2011).

[44] Yu. Gorbachev, O. Kunova, G. Shoev. Phys. Fluids, **33**, 126105 (2021). DOI: 10.1063/5.0062628.

[45] V.N. Kondratiev, E.E. Nikitin. *Gas-Phase Reactions: Kinetics and Mechanisms* (Springer, Berlin, 1981), DOI: 10.1007/978-3-642-67608-6

[46] *NIST, National Institute of Standards and Technology, Chemical Kinetics Database,* http://kinetics.nist.gov/kinetics/index.jsp

[47] P.A. Vlasov, V.N. Smirnov, A.M. Tereza. Russ. J. Phys. Chem. B, **10**, 456 (2016). DOI: 10.1134/S1990793116030283

[48] D. Cecere, E. Giacomazzi, A. Ingenito. Int. J. Hydrogen Energy, **39**, 10731 (2014). DOI: 10.1016/j.ijhydene.2014.04.126

[49] N.N. Smirnov, V.F. Nikitin. Int. J. Hydrogen Energy, **39**, 1122 (2014). DOI: 10.1016/j.ijhydene.2013.10.097

[50] P. Sharma, A. Dhar. Int. J. Hydrogen Energy, **41**, 6148 (2016). DOI: 10.1016/j.ijhydene.2015.12.021

[51] R.K. Maurya, N. Akhil. Int. J. Hydrogen Energy, **42**, 11911 (2017). DOI: 10.1016/j.ijhydene.2017.02.155

[52] B. Liu, G-Q. He, F. Qin, J. An, S. Wang, L. Shi. Int. J. Hydrogen Energy, **44**, 5007 (2019). DOI: 10.1016/j.ijhydene.2019.01.005

[53] V.N. Kondratiev. V sb. *Problemy khimicheskoj kinetiki (K vos'midesyatiletiyu akademika N.N. Semenova)*, pod. red. V.N. Kondratieva (Nauka, M., 1979), s. 13. (in Russian)

[54] A. Fernandes-Ramos, J.A. Miller, S.J. Klippenstein, D.G. Truhlar. Chem. Rev., **106**, 4518 (2006). DOI: 10.1021/cr050205w

[55] R.L. Wadlinger, B.deB. Darwent. J. Phys. Chem., **71**, 2057 (1967). DOI: 10.1021/j100866a013

[56] R.T. Pack, E.A. Butcher, G.A. Parker. J. Chem. Phys., **102**, 5998 (1995). DOI: 10.1063/1.469334

[57] A.J. Dobbyn, M. Stumpf, H-M. Keller, R. Schinke. J. Chem. Phys., **104**, 8357 (1996). DOI: 10.1063/1.471587

[58] L.B. Harding, J. Troe, V.G. Ushakov. Phys. Chem. Chem. Phys., **2**, 631 (2000). DOI: 10.1039/a908929b

[59] D. Rapp, T. Kassal. Chem. Rev., **69**, 61 (1969). DOI: 10.1021/cr60257a003

[60] A.S. Biryukov, B.F. Gordiets. PMTF, **6**, 29 (1972). (in Russian)

[61] E.E. Nikitin, A.I. Osipov. *Kolebatel'naya relaksatsiya v gazakh. Itogi nauki i tekhniki. Ser. Kinetika i kataliz* (VINITI, M., 1977), t. 4. (in Russian)

[62] N.M. Kuznetsov. *Kinetika monomolekulyarnykh reaktsij* (Nauka, M., 1982) (in Russian)

[63] O.V. Skrebkov. Chem. Phys., **191**, 87 (1995). DOI: 10.1016/0301-0104(94)00303-R

[64] S.P. Karkach, V.I. Osherov. J. Chem. Phys., **110**, 11918 (1999). DOI: 10.1063/1.479131

[65] S.P. Karkach, V.I. Osherov, V.G. Ushakov. Chem. Phys. Reports, **19** 10, 1777 (2001).

[66] J. Troe, V.G. Ushakov. J. Chem. Phys., **128**, 204307 (2008). DOI: 10.1063/1.2917201

[67] Z. Sun, D.H. Zhang, C. Xu, S. Zhou, D. Xie, G. Lendvay, S-Y. Lee, S.Y. Lin, H. Guo. J. Am. Chem. Soc., **130**, 14962 (2008). DOI: 10.1021/ja8068616

[68] M. Jorfi, P. Honvault, P. Bargueno, T. Gonzalez-Lezana, P. Larregaray, L. Bonnet, P. Halvick. J. Chem. Phys., **130**, 184301 (2009). DOI: 10.1063/1.3128537

[69] P. Szabo, G. Lendvay. J. Phys. Chem. A, **119**, 12485 (2015). DOI: 10.1021/acs.jpca.5b07938

[70] N.V. Evtyukhin, S.V. Kulikov, V.M. Vasil'ev, A.P. Genich, G.B. Manelis, O.V. Skrebkov. V sb.: *Khimicheskaya fizika goreniya i vzryva. Kinetika khimicheskikh reaktsij. Materialy V Vsesoyuznogo simpoziuma po goreniyu i vzryvy* (Chernogolovka, 1977), s. 5. (in Russian)

[71] A.P. Genich, N.V. Evtyukhin, S.V. Kulikov, G.B. Manelis, M.E. Solovieva. PMTF, **1**, 34 (1979). (in Russian)

[72] N.V. Evtyukhin, S.V. Kulikov, M.E. Solovieva. PMTF, **6**, 4 (1982). (in Russian)

[73] S. Chapman, T.G. Cowling. *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, UK., Cambridge, 1952)

[74] N.M. Kuznetsov. DAN USSR, **202** (6), 1367 (1972). (in Russian).

[75] S.A. Losev. Fizika goreniya i vzryva, **6**, 767 (1973). (in Russian)

[76] O.V. Skrebkov, S.P. Karkach, V.M. Vasil'ev, A.L. Smirnov. Chem. Phys. Lett., **375**, 413 (2003). DOI: 10.1016/S0009-2614(03)00875-3

[77] S.-O. Ryu, S.M. Hwang, M.J. Rabinovitz. J. Phys. Chem., **99**, 13984 (1995). DOI: 10.1021/j100038a033

[78] E.L. Petersen, D.M. Kalitan, M.J.A. Rickard. J. Propulsion and Power, **20**, 665 (2004). DOI: 10.2514/1.11380

[79] R. Mevel, S. Pichon, L. Catoire, N. Chaumeix, C-E. Paillard, J.E. Shepherd. *Proceedings of the 34th International Symposium on Combustion* (Warsaw, Poland, July 29 August 3 2012)

[80] V.A. Pavlov, O.P. Shatalov. Kinetics and Catalysis, **52** (2), 157 (2011). DOI: 10.1134/S0023158411020157

[81] J.A. Miller, R.J. Kee, C.K. Westbrook. Annu. Rev. Phys. Chem., **41**, 345 (1990). DOI: 10.1146/annurev.pc.41.100190.002021

[82] *Termodinamicheskie svojstva individual'nykh veschestv,* pod red. V.P. Glushko (Nauka, M., 1978) (in Russian)

[83] R. Shaw. Int. J. Chem. Kin., **9**, 929 (1977). DOI: 10.1002/kin.550090608

[84] K.F. Herzfeld, T.A. Litovitz. *Absorbtion and Dispersion of Ultrasonic Waves* (Acad. Press, N.Y.L., 1959)

[85] C.B. Moore. J. Chem. Phys., **43**, 2979 (1965). DOI: 10.1063/1.1697261

[86] S. Ormonde, Rev. Mod. Phys., **47** (1), 193 (1975). DOI: 10.1103/RevModPhys.47.193

[87] A.V. Eletskiy. UFN, **134** (2), 237 (1981). (in Russian). DOI: 10.3367/UFNr.0134.198106b.0237

[88] A. Kosareva, E. Kustova, M. Mekhonoshina. Plasma Sources Sci. Technol., **31**, 104002 (2022), DOI: 10.1088/1361-6595/ac91f2

[89] I. Adamovich, S. Macheret, J. Rich, C. Treanor. J. Thermophys. Heat Transfer, **12**, 57 (1998). DOI: 10.2514/2.6302

[90] O.V. Skrebkov, A.L. Smirnov. Sov. J. Chem. Phys., **10** (8), 1598 (1992).

[91] A.L. Smirnov, O.V. Skrebkov. Sov. J. Chem. Phys., **11** (1), 51 (1992).

[92] I.A. Konovalova, S.Ya. Umanskii. Khimicheskaya fizika, **1** (7), 901 (1982). (in Russian)

[93] G.L. Schott, R.W. Getzinger. In: *Physical Chemistry of Fast Reactions, Gas Phase Reactions of Small Molecules* (London, Plenum, 1973), v. 1, p. 81.

[94] F.E. Belles, M.R. Lauver. J. Chem. Phys., **40**, 415 (1964). DOI: 10.1063/1.1725129

[95] G.B. Skinner, G.H. Ringrose, J. Chem. Phys., **42**, 2190 (1965). DOI: 10.1063/1.1696266

[96] Y. Hidaka, S. Takahashi, H. Kawano, M. Suga, W.C. Gardiner Jr.. J. Phys. Chem., **86**, 1429 (1982). DOI: 10.1021/j100397a043

[97] P.W. Fairchild, G.P. Smith, D.R. Crosley. J. Chem. Phys., **79**, 1795 (1983). DOI: 10.1063/1.446025

[98] G.P. Smith, D.R. Crosley. J. Chem. Phys., **85**, 3896 (1986). DOI: 10.1063/1.450910

[99] L.P. Dempsey, C. Murray, M.I. Lester. J. Chem. Phys., **127**, 151101 (2007). DOI: 10.1063/1.2800316

[100] L.P. Dempsey, T.D. Sechler, C. Murray, M.I. Lester. J. Phys. Chem. A, **113**, 6851 (2009). DOI: 10.1021/jp902935c

[101] M. Brouard, J. Lawlor, G. McCrudden, T. Perkins, S.A. Seamons, P. Stevenson, H. Chadwick, F.J. Aoiz. J. Chem. Phys., **146**, 244313 (2017). DOI: 10.1063/1.4989567

[102] R.R. Baldwin, N.S. Corney, R.M. Precious. Nature, **169**, 201 (1952). DOI: 10.1038/169201b0

[103] R.R. Baldwin, R.F. Simmons. Trans. Faraday Soc., **51**, 680 (1955). DOI: 10.1039/TF9555100680

[104] R.R. Baldwin, R.F. Simmons. Trans. Faraday Soc., **53**, 955 (1957). DOI: 10.1039/TF9575300955

[105] R.R. Baldwin, D.W. Cowe. Trans. Furaday Soc., **58**, 1768 (1962). DOI: 10.1039/TF9625801768

[106] R.R. Baldwin, R.F. Simmons, R.W. Walker. Trans. Faraday Soc., **62**, 2476 (1966). DOI: 10.1039/TF9666202476

[107] V.V. Azatyan, V.A. Pavlov, O.P. Shatalov. Kinetics and Catalysis, **46** (6), (2005). DOI: 0.31857/S0453881120030041

[108] V.V. Azatyan, Yu.N. Shebeko, I.A. Bolod'yan, A.Yu. Shebeko, V.Yu. Navtsenya, A.V. Tomilin. Khimicheskaya fizika, **27** (7), 72 (2008). (in Russian)

[109] N.M. Rubtsov, B.S. Seplyarskii, A.P. Kalinin, K.Ya. Troshin. ZhTF, **91** (6), 895 (2021). (in Russian) DOI: 10.21883/JTF.2021.06.50857.269-20

[110] S.A. Losev, V.N. Makarov, V.A. Pavlov, O.P. Shatalov. Fizika goreniya i vzryva, **9** (4), 463 (1973). (in Russian)

[111] A.S. Biryukov, A.Yu. Volkov, A.I. Demin, E.M. Kudryavtsev, Yu.A. Kulagin, N.N. Sobolev, L.A. Shelepin. ZhETF, **68** (5), 1664 (1975). (in Russian).

[112] J.D. Lambert, R. Salter. Proc. Roy. Soc., **A253**, 277 (1959). DOI: 10.1098/rspa.1959.0193

[113] R. Holmes, G.R. Jones, N. Pusat. J. Chem. Phys., **41** (8), 2512 (1964). DOI: 10.1063/1.1726296

[114] R.C. Millican, D.R. White. J. Chem. Phys., **39**, 3209 (1963). DOI: 10.1063/1.1734182

[115] L. Landau, E. Teller. Phys. Z. Sow., **10**, 34 (1936).

[116] J.C. Keck, G. Carrier. J. Chem. Phys., **43**, 2284 (1965). DOI: 10.1063/1.1697125

Translated by I.Mazurov