Journal of Engineering Physics and Thermophysics, Vol. 70, No. 3, 1997

ON A SIMPLIFIED MODEL OF CHEMICAL KINETICS NEAR THE DETONATION LIMITS

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UDC 534.222.22

Results of using the simplified Korobeinikov–Levin two-parameter model of chemical kinetics to determine parameters behind a reflected shock wave in shock-tube experiments are discussed.

Introduction. The detailed kinetic scheme for combustion of such a "simple" fuel as hydrogen in air includes 9 components and more than 50 elementary reactions [1-4]. Even for the binary $H_2 + O_2$ mixture the basic scheme of reactions needs no less than 8 reactive species (H, O, H_2, O_2, OH, H_2O, HO_2, H_2O_2) and 17 elementary chemical reactions. Therefore it is urgent to choose a simplified, as much as possible, kinetics model which, would nevertheless be adequate to the complete scheme with respect to time and energy characteristics of the reactions as well as to the integral parameters of energy release.

Such a simple model for the spatial structure of a detonation wave of combustion was suggested at the end of the 1960s [5-7], which is now known as the Korobeinikov–Levin two-parameter (K-L) model. This model allows correctly both for the final rate of chemical reactions and for the incomplete combustion of a reactive mixture behind the wave front when due to a high temperature the mixture burns incompletely, thus releasing thermal energy only partially. The role of the reverse reaction has been elucidated; until recently it has been ignored in describing gas motion behind a detonation wave.

Such an approach as a whole allows the extremely cumbersome general problem on determination of the motion of reacting systems to be separated into two, namely, kinetic and gasdynamic, thus simplifying considerably construction of a solution where such a separation is justified.

The present work provides results of a consideration of the methods of selection of coefficients for the K-L model for chemical kinetics of the stoichiometric mixture $H_2 + O_2/2 : 1$ and their use in numerical simulations of detonation with subsequent direct comparison of calculated data and results of shock-tube experiments.

Model and Technique. In accordance with [5, 6], instead of a detailed kinetic scheme of elementary reactions, we adopt a parametric two-step model involving chemical reactions with heat release behind the wave front after passage of the induction period characterized by only two components. The first component, c, stands for the delay of heat release due to the finite rate of the chemical chain branching and propagation reactions in the preflame relatively low-temperature field [1, 6], where active centers (radicals), i.e., chain-carriers, are formed. Then the equation of the first step acquires the form

$$\frac{dc}{dt} = -\varphi(x, t)/\tau_{\text{ind}}, \tag{1}$$

where $\varphi(x, t)$ is a function in general form that takes into account the prehistory, i.e., the initial space distribution of radicals behind the incident wave at some moment of time; τ_{ind} is the induction period in the medium calculated by the parameters behind the incident wave. Equation (1) is solved simultaneously with the transfer equations, where the component c is considered as an inert admixture transferred by convection, which does not exert a direct influence on the gasdynamical parameters. The second component, β, describes heat release. The equation of the second step is of the form

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Academic Scientific Complex "A. V. Luikov Heat and Mass Transfer Institute of the Academy of Sciences of Belarus," Minsk, Belarus. Translated from Inzhenerno-Fizicheskii Zhurnal Vol. 70, No. 3, pp. 428-435, May-June, 1997. Original article submitted December 6, 1996.

TABLE 1. Coefficients for τ_{ind} in (3) for $H_2 : O_2/ 2 : 1$ Stoichiometric Composition for Pressure $0.1 < P_0 < 50$ atm and Temperature $900 < T_0 < 2000$ K

K_l	l_l	n_l	$\rho E_k/P$	Refs.
$52.88 \cdot 10^{-4}$	0.464	0	$5.055 \cdot 10^6/(P/\rho)$, J/kg	A_1 [14]
$4.54 \cdot 10^{-4}$	0.987	0	$6.346 \cdot 10^6/(P/\rho)$, J/kg	A_2 [14]
$3.5 \cdot 10^{-4}[H_2]^{-0.8}[O_2]^{-0.92}$	0	1	$22.000/T$	A_6 [1]
$5.606 \cdot 10^{-5}/T$, K	0	1	$15{,}200/RT$, kcal/mole	A_3 [8]
$1/300$	1	0	$9800/T$	A_4 [9]
$1/850.32$	1	0	$5.845 \cdot 10^6/(P/\rho)$, J/kg	A_5 [12]
$2.30 \cdot 10^{-2}$	0	1	$7550/T$, K	$T > 1200$ K [1]
$5.0 \cdot 10^{-30}$	0	1	$69{,}800/T$, K	$T < 900$ K [1]

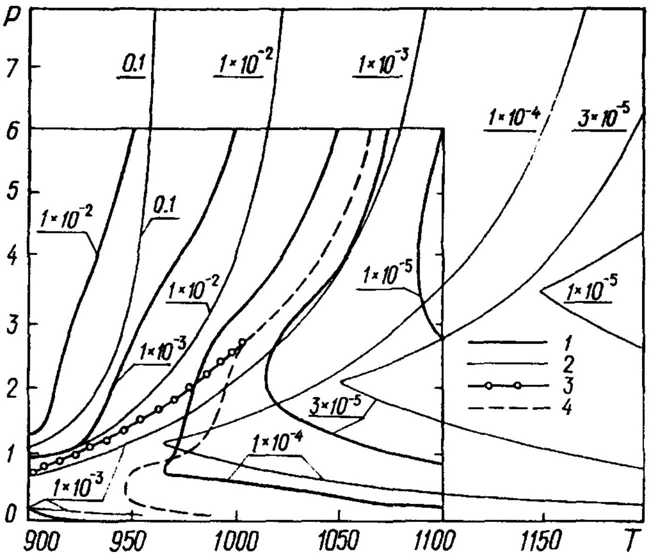

Fig. 1. Comparison of induction times (sec) for $H_2 : O_2/2 : 1$ mixture: 1, 2) constant value of the induction time (1, data [3], 2, present work); 3) second expanded ignition limit [16]; 4) separation of strong and weak ignition regions [4].

$$\frac{d\beta}{dt} = -\beta^m/\tau_2 + (1-\beta)^m/\tau_3, \quad \text{if} \quad c < c_1 ; \tag{2}$$

$$1/\tau_k = K_k \rho^{l_k} P^{n_k} \exp\left[-\rho E_k/P\right], \quad k = 1 \text{ (ind)}, 2, 3 . \tag{3}$$

The coefficients in Arrhenius dependences (3) for the induction period τ_{ind} and characteristic times of energy release for direct (τ_2) and reverse (τ_3) reactions of the entire process can be chosen by different methods, provided their use allows time variation of the gasdynamical parameters of the medium which is in the best agreement with experimental data or calculations made using detailed kinetic schemes of reactions (see [12-14]). Coefficients for a mixture with the stoichiometric composition $H_2 : O_2/2 : 1$ [14] and those selected in [12] for pressure $0.1 < P_0 < 50$ atm and temperature $900 < T_0 < 2000$ K are given in Table 1.

TABLE 2. Ignition Time Delays Obtained for Different Experimental Data at a Point ($P_0 = 1$ atm), $T_0 = 1000$ K)

$\tau_{ind}(P_0, T_0)$	Refs.	$\tau_{ind}(P_0, T_0)$	Refs.
43.8	A_1 [14]	64.3	A_6 [1]
78.8	A_2 [14]	$80 < \tau < 400$	experiment [15]
118.18	A_3 [8]	$40 < \tau < 300$	experiment [13]
409.9	A_4 [9]	92.23	calculation [12]
85.1	A_5 [12]	85.11	approximation (5)
≈ 130	$H_2{:}O_2{:}N_2/2 : 1 : 4$ [3]	$\approx 56.$ $(30 < \tau < 100)$	$H_2{:}O_2/2{:}1$ [3]

A comparison of our data on the induction period with the data of other authors, in particular, [3, 4] is made in [12, 13]. Within the temperature range $T_0 > 1600$ K, the data coincide practically completely in the entire pressure range under consideration. The difference increases with decreasing T and with increasing P.

A direct graphical superposition of our data, obtained using approximate relations for the calculated delay times in the problem based on the detailed kinetic scheme, onto those given in [3] for the $H_2 : O_2/2 : 1$ mixture in the ranges $0.1 < P_0 < 6$ atm and $900 < T_0 < 1100$ K has shown already a discrepancy (of about 10%) at pressures exceeding 0.5 atm, which reaches an order of magnitude at $P = 6$ atm (see Fig. 1). Thus, the greatest discrepancy occurs in the transition zone when the kinetic mechanism of the leading reactions changes, and, in particular, the role of trimolecular reactions of HO_2 radical formation becomes more significant.

On the Accuracy of the Approximations. A comparison of the τ_{ind} values obtained by different authors at points typical for practical applications in the region of variation of the parameters has revealed the necessity of selecting the coefficients in (2) separately for low- and high-pressure regions on the parametric curve $T_0 =$ const with subsequent asymptotic matching of their values in the transition zone. In [14] no such separation of subregions was made; therefore, the dependences obtained can actually be used, as can the data from [5-11], only in a high-temperature low-pressure region.

The accuracy of different approximations can be judged by the scatter of the delay times obtained in the neighborhood of some point of practical interest in this subregion which could be adopted as the normalization point, e.g., with the parameters $P_0 = 1$ atm and $T_0 = 1000$ K. The corresponding data are given in Table 2. Their analysis allows us to unambigously conclude that almost all the approximate dependences give values within the scatter limits of the experimentally measured delay times [12, 15-17]. Table 2 also includes refined experimental data obtained in [12] in the neighbourhood of the normalization point. Their approximation for different sets of data by relations of the Arrhenius type (similarly to those given in Table 1) with a scatter of ± 35% yields values of from 137 to 232 msec at the considered point. In this case, neglect of the temperature dependence of the adiabatic exponent (or the molecular weight) for incident or reflected shock waves leads to a 3–5% decrease in the pressure and temperature values and to almost a 1.5-fold increase in the calculated τ_{ind}.

It should be noted that the activation energy in the empirical dependences approximating the experimental data in Table 2 initially ranges from 28 to 30 kcal/mole. It is consistent with the results of [17] for the same conditions (30 kcal/mole), 1.5-fold higher than that (19.6 kcal/mole) in [7, 9-11], and almost twice (15.2 kcal/mole) he activation energy in [8, 17], where the kinetic parameters were chosen to ensure better correspondence of the measurement conditions of ignition delays to those in the induction zone of the detonation wave, thus allowing the limiting diameter and the length of the reaction zone to be calculated with a 5% error within the detonation limit.

In this connection, we determined the change in the activation energy in the zone of branched chain reactions as a function of temperature from the calculation data based on the detailed kinetics [12], and obtained the following relations for the parameters in (3):

TABLE 3. Experimental Data Near the Calibration Point ($P_0 = 1$ atm, $T_0 = 1000$ K) for Gas with Initial Parameters P_1, $T_1 = 291.15$ K in Front of the Incident Shock Wave and with P_5, T_5 Behind That Reflected from a Flat Wall. Induction Time: τ_{ind}^{exp} – Experiment [13], τ_{ind}^{appr} – Calculation by Arrhenius Approximation (3), and $\tau_{ind}^{num.appr}$ – Calculation by Numerical Approximation (5)

Experiment No.	V_1	P_1, Torr	P_5, atm	$T_5/1000$	τ_{ind}^{exp}, μsec	τ_{ind}^{appr}, μsec	$\tau_{ind}^{num.appr}$, μsec
E01	1447.5	21.80	1.1633	1.1791	33.0	32.7	28.3
E02	1428.5	23.51	1.2067	1.1538	39.0	38.9	30.9
E03	1418.7	25.62	1.2886	1.1409	44.0	40.8	31.0
E04	1373.6	24.94	1.1395	1.0824	73.0	79.3	47.1
E05	1373.6	24.72	1.1294	1.0824	71.0	80.0	47.5
E06	1373.6	24.32	1.1111	1.0824	78.0	81.3	48.2
E07	1369.9	23.61	1.0700	1.0777	–	88.4	51.2
E08	1362.4	25.50	1.1368	1.0682	83.0	91.5	51.2
E09	1353.5	25.60	1.1190	1.0570	102.0	104.2	55.4
E10	1342.9	26.82	1.1448	1.0437	106.9	116.9	58.6
E11	1344.8	24.40	1.0460	1.0461	108.0	124.8	62.7
E12	1324.1	24.94	1.0201	1.0204	183.0	168.6	75.0
E13	1324.8	26.50	1.0856	1.0213	215.0	156.9	70.6
E14	1317.8	23.90	0.9634	1.0127	220.0	194.5	82.9
E15	1315.0	24.74	0.9909	1.0093	275.0	196.5	82.7
E16	1320.0	25.20	1.0208	1.0153	274.0	178.4	77.5
E17	1319.9	25.20	1.0208	1.0153	276.0	178.4	77.5
E18	1310.3	25.25	1.0000	1.0035	–	207.9	85.1
E19	1295.3	25.00	0.9561	0.9854	374.0	268.4	99.9
E21	1279.4	26.38	0.9713	0.9663	441.0	332.4	112.3
E22	1253.2	26.86	0.9277	0.9354	545.0	515.4	146.4

Note: $\gamma_1 = 1.39765$, $\gamma_2 = 1.374$, $\gamma_3 =$ var; $\rho_1 =$ var, $\mu_1 = 12.01$; $\rho_2 = P_2/(R_0T_2/\mu_2)$; $\mu_2 = 12.4389$; $\rho_5 =$ var, $\mu_5 =$ var; τ_{ind}^{appr} [μsec] $= 0.767\cdot 10^5 \rho$ [kg/m^3] $\exp(-9.824\cdot 10^6/(P/\rho))$ [J/kg].

$$x = \frac{T}{1000}, \quad 0.9 \le x \le 5\,, \quad l_1 = 0\,, \quad n_1 = 0.9x^{0.076} = 0.893 \div 1.017\,;$$

$$K_1\ [\mathrm{atm}^{-n_1}\ \mathrm{sec}^{-1}] = 10^{8+n_1}\,, \quad E_1(T)\,T = 6980/x^{0.14} = 7085 \div 5570\,. \tag{4}$$

Thus, in the region of chain reactions with an increase in temperature the effective activation energy changes, in accordance with the model based on the detailed mechanism of chemical reactions, from 4.74 to 3.72 MJ/kg (or from 11 to 14 kcal/mole), which is 2-3-fold smaller than for similar dependences used in approximating the experimental data given in Table 2.

On a Criterion for Determination of the Detonation Limits. While in determination of the detonation limits the mere fact that the detonation wave is absent beyond the detonation limit can be used [1-4, 17], in the zone of

TABLE 4. Comparison of Calculated and Experimental Readings of Pressure Transducers for Incident, Reflected, and Detonation Shock Waves

Designation	V_1	P_0, Torr	t_B, μsec	t_C, μsec	t_B^{det}, μsec	t_C^{del}, μsec	t_D^{del}, μsec
Experiment E01	1447.5	21.80	66	–	100	109	140
Calculation	–	–	66.3	112	102.6	113	140.6
Experiment E05	1373.6	24.72	71	118	143	149	172
Calculation	–	–	69.7	124	144.3	148.9	171.9
Experiment E08	1362.4	25.50	72	118	160	162	185
Calculation	–	–	70.1	120	153.5	160.5	183.4
Experiment E09	1353.5	25.60	71	118	159	163	185
Calculation	–	–	70.6	120.8	160	164.3	186.4
Experiment E11	1344.8	24.20	70	117	185	189	208
Calculation	–	–	71.2	124	185	191.9	209

transition through the chain limit we have only a marked increase in the delay time of ignition. As for the existence of a detonation wave, this fact is beyond question [15-17]. Therefore, the boundary of such limits can be determined rather arbitrarily.

In [17], in determining the main kinetic scheme of reactions an account has been made of the considerable excess of the effective activation energy (30 kcal/mole) over its values in the majority of elementary reactions, and the condition of chain initiation by heat according to the scheme $H_2 + O_2 \rightarrow OH + OH$ with $Q = 45$ kcal/mole was used.

As the leading reaction, the branching reaction $H + O_2 \xrightarrow{k_2} OH + O$, with k_2 [cm^3/sec] $= 5.35 \cdot 10^{-12} T^{0.5} \exp(-18{,}000/RT)$ was adopted. In this case, the values of τ_{ind} as a function of the initial temperature calculated in the range $T = 1100-2000$ K at $P = 1$ atm were in good agreement with the experimental data of [15-17].

With a decreasing initial temperature and increasing pressure, the reaction of free valence capture following the scheme $H + O_2 + M \xrightarrow{k_3} H_2O + M$ became dominant and the boundary was determined as the condition of reaching the capture-to-branching reaction rate ratio $\omega_3/\omega_2 \approx 10^{-5}$ [15, 16]. In this case, the calculated and experimental data were in fair qualitative agreement, however the scatter of the experimental τ_{ind} values against the calculated dependence was more than an order of magnitude [16]. For the region of the chain reaction the following approximation of the delay time was obtained:

$$\log_{10} \tau_{ind}\ [\mu\text{sec}] = 0.9x^{0.076}\,(1 - \log_{10} P\ [\text{atm}]) + 3.03x^{-1.14} - 2\,,$$

$$0.9 \le x = \frac{T}{1000} \le 5\,,\quad 0.1 \le P \le 50\ \text{atm}\,, \tag{5}$$

which provided no more than 10% deviation from the calculated values obtained using the detailed scheme. Thereafter, the boundary of the chain limit was determined as the set of points at which with an increase in P the deviation of τ_{ind} at $T_0 = \text{const}$ exceeded 10%. For boundary values of the parameters we obtained the following approximate dependences for the upper (P^{**}) and lower (P^{*}) pressure bounds, respectively:

$$\log_{10} P^{**} = 0.84044 + 0.17786\,x + 0.043x^2\,,\quad 0.9 < x < 1.65\,,$$

$$\log_{10} P^{*} = -\,10.3018 + 21.1906x - 13.9415x^2 + 3.23618x^3\,,\quad 0.9 < x < 5\,; \tag{6}$$

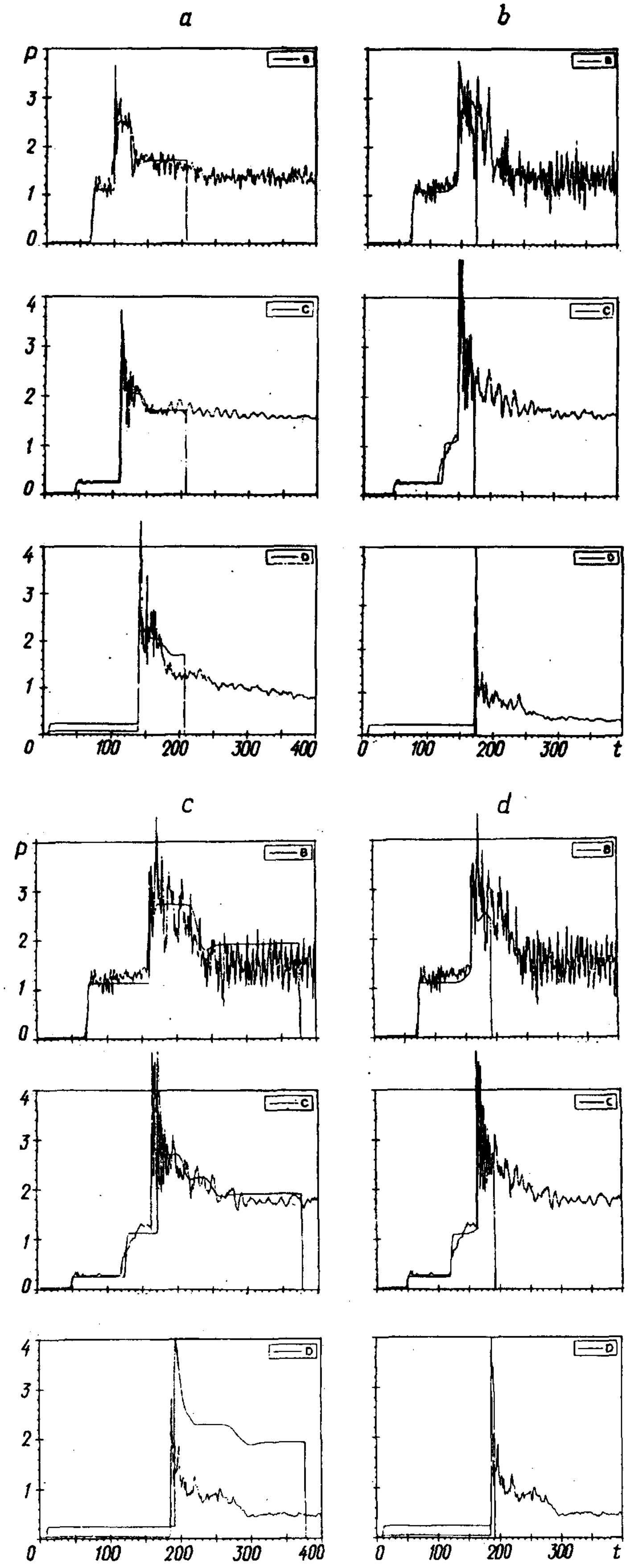

Fig. 2. Comparison of calculation and experiment from pressure oscillograms: a) experiment E01; b) E05; c) E08; d) E09. P, atm; t, μsec.

At $T_0 = 1000$ K we have $P^* = 1.526$ atm, which means that the point chosen as the normalization one from the data calculated using the detailed scheme must lie outside the chain-limit zone. From (6) for the delay time we obtain τ_{ind} ($P_0 = 1$ atm, $T_0 = 1000$ K) = 85.11 μsec, which differs by 8.5% from the 92.3 μsec calculated using the detailed scheme and is 1.6–2.7-fold lower as compared to the ignition delay obtained in different interpolations of experimental data (see Table 2). Approximate dependences for the region of the chain limit and higher are given in [12]. Note that P^* ($T = 1200$ K) = 4.40 atm; P^* ($T = 1600$ K) = 14.7 atm; P^* ($T = 2000$ K) = 160 atm.

Results of Numerical Simulations. Tables 3 and 4 and Fig. 2d give the results of comparison of the calculated (numerical simulation with use of the Yee–Harten TVD method and the TVD modification for coarse particles developed by Yu. M. Davydov [14]) and experimental data on reflection of shock waves from a flat rigid wall followed by development of detonation near the wall behind the reflected wave ($M_1 = 2.5$–2.7).

In the comparisons, we employed oscillograms recorded by pressure transducers placed on the end face (index B) and on the side surfaces of the shock tube at distances of 30 mm (index C) and 82 mm (index D), respectively, from the end of the tube [13]. The zero time reference in the calculations ensured coincidence of the time marks for the incident shock wave up to the moment of reflection with an accuracy of up to 2% of the running time (within the limits of 1–2 μsec). For the reflected shock wave, the deviation from the experimental data increased to 6% (within the limits of up to 10 μsec, see Table 4). Recording of the moments of passage of detonation waves (additional index "det") by the transducers provided an accuracy of 6% of the instantaneous time (up to 10 μsec).

Matching of the time marks of initiation and development of detonation followed by propagation of a detonation wave necessitated the use of more exact dependences for $\gamma(\rho, P/\rho)$ and $T(P/\rho, \mu)$. Errors of 3–5% in temperature determination resulted in a change in the detonation wave velocity, determined by time marks, in the range of 10–20 μsec (10–25%), and in the delay period, of up to 50% as compared to experimental values.

In these conditions, a change in the parameters of energy release (in Eq. (3)) exerted an influence mainly not only on the stationary velocity of the detonation wave, traveling in the medium with parameters of the incident shock wave, but also on the levels of pressure "plateau" developed before and after interaction of fronts of the detonation and reflected waves.

For the considered period of time, not exceeding 400 μsec, the scatter in the readings upon changing the rate of energy release or incomplete combustion was about ±8 μsec. In this case, we controlled the deviation of the pressure levels behind the detonation wave, which did not exceed 10–15% of the mean value of experimental data. As by the time of energy release the delay period was already determined at each calculated point of flow, it was convenient, following [6, 7], to use τ_{ind} as the normalization parameter in (3) for the purpose of more exact determination of preexponential values in the course of matching. Then, instead of (2), (3), we arrived at

$$\frac{d\beta}{dt} = \frac{1}{\alpha_2 \tau_{\text{ind}}} \exp\left(\rho \frac{E_1}{P} (E_2/E_1 - 1)\right) [(1-\beta)^2 \exp(\rho q/P) K - \beta^2], \tag{2'}$$

$$K_1 \rho = \exp(\rho E_1/P)/\tau_{\text{ind}} = \alpha_2 K_2 P^2, \tag{3'}$$

where α_2 determines the effective portion of molecular collisions resulting in energy release; $K = K_2/K_3$ is the preexponential of the effective gross reaction; $q = E_2 - E_3$. The value of α_2 varied from 6 to 8000 and in the last approximations was assumed equal to 12.24. The parameter K ranged from 1 to 200 and in the last approximations was $K = 7.8$; $E_1 = 6.346$ MJ/kg, $E_2 = 2$ MJ/kg, and $E_3 = 7$ MJ/kg [8-11].

NOTATION

P, pressure, atm; T, temperature, K; ρ, density, kg/m^3; c, first component in the K-L model; β, second component in the K-L model for heat release; $\varphi(x, t)$, function of the coordinate (x) and time (t) in general form with allowance for the prehistory, i.e., initial space distribution of radicals behind the incident wave within some moment of time; τ_{ind}, induction period calculated by the parameters behind the incident wave; γ, adiabatic exponent; μ, molecular weight; E_k, activation energy (J/kg), and K_k, l_k, n_k, coefficients in Arrhenius approximations (3); α_2, K, and q, parameters in (2'); A_1 ... A_6, indicate the corresponding sets of data in Tables 1, 2; V_1, velocity of the incident shock wave, m/sec (in Table 4); R_0, gas constant. Subscripts : 1 and ind, for induction period; 2 and 3, straight (τ_2) and reverse (τ_3) entire-process reactions; $k = 1$ (ind), 2, 3; $m = 2$; $c_1 = 0.9-0.99$.

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