Harbingers of dioxins in thermal decomposition of high-energy fuel

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Abstract. Combustion of high-energy chemical fuels containing dioxins in their elemental composition can lead to the formation of super eco toxicants on smoke particles - polychlorinated dioxins and furans. The choice of the method of solving the equations of chemical kinetics is basic in numerical experiment. Calculation and theoretical studies were carried out to solve the problem of determining the parameters of combustion products of chemical fuels taking into account the formation of traces of polychlorinated dioxins. Basic information on the adopted method of determining non-equilibrium composition of combustion products of chlorine-containing chemical fuels is presented. Based on the literary analysis on the mechanisms and rates of chemical reactions of conversion of chlorine-containing compounds, a kinetic model of formation of traces of dioxins was built. Numerical calculations on the assumption of chemical equilibrium have shown that the dioxins formation process is substantially non-equilibrium. The results of kinetic studies on the emission of dioxins precursors showed the nature of the change in time of various components of combustion products of chemical fuels depending on temperature.

Keywords: combustion, dioxins, emission, properties, fuel, thermal decomposition.

1 Introduction

Dioxins on particles of the smoke, which is formed at combustion of chemical fuels, is found nearly a quarter of the century back. However, despite numerous laboratory and natural researches there is no complete quantitative description of processes of formation and disintegration of the polychlorinated dioxins, furans, and biphenyls now. Concentration of the dioxins, which is formed at combustion of chemical fuels, is usually small, and the published results of researches have broad dispersion in the measured concentration. As formation of dioxins is only insignificant collateral reaction in the general process of decay and synthesis of organic compounds, interpretation of experimental results is a difficult procedure in comparison with researches of the main reactionary process [1-4].

Establishment of distribution of chlorine atoms in dibenzene - \( p \) - dioxins was important result of the analysis of composition of dioxins on smoke particles (the solid condensed particles). In most cases, stronger chlorinated connections are more preferably formed, and often the maximum of distribution corresponds six replacements with chlorine atoms of hydrogen atoms. In certain cases, oktochlorinated connections are preferable. Isomer 2, 3, 7, 8 – tetra chlorine dibenzene - \( p \) - dioxins is formed not in the largest number. There is no standard theoretical model of the mechanism of formation of dioxins reproducing observed distribution yet. It is connected in particular with difficult enrollment of the physical and chemical processes proceeding in combustion chambers for combustion of chemical fuels [5-7].

Formation of dioxins happens in the temperature range 500...800 \( K \) [6-8]. In the presence of particles of smoke, chlorine and at excess of oxygen, many aromatic connections can form...
connections of type of dioxins with the corresponding distribution on family of the chlorine-replaced dioxins. The chlorinated phenols and the high-chlorinated aromatic air can be the most probable harbingers. Experiments show that the formation of dioxins most often occurs when pentachlorophenol ($C_6Cl_5OH$) is present [9-11].

Low level of temperatures of dioxins formation demands accounting of kinetic factors. Uncertainty as a part of reactionary mixture, in properties of particles of smoke, kinetics of pyrolysis and chemical stability of connections have a great influence on reliability of forecasting of emission of dioxins by methods of chemical kinetics under the considered conditions.

It is necessary for determination of the regime parameters providing the minimum exit of dioxins, reliable forecasting of structure and properties of products of chemical fuels [12]. The solution of an objective demands attraction of the advanced methods and the latest developments of many sciences: chemical kinetics and thermodynamics, gas dynamics and heat exchange, kinetics of phase transformations, molecular and kinetic theory of gases and liquids. It is connected with the fact that real process of combustion of chemical fuels represents the difficult process which is carried out in the wide range of temperature, times of stay in reaction and includes a large amount of various substances [13], [14]. With oxidizing reactions also pyrolytic can proceed. The description of evolution in time of various substances requires reliable definition of entry conditions that often cannot be made. The problem is complicated also by the fact that now there is no complete quantitative description of formation and disintegration of dioxins [15]. The published experimental results often have considerable dispersion in concentration of dioxins. Perhaps, it is connected with the fact that formation of dioxins is only insignificant collateral reaction in the general process of disintegration of organic matter. Therefore, based on the available experimental data, it is difficult to reliably present the mechanism of chemical reactions as well as their rate constants.

Measurement of concentration of various products of combustion on a path of propulsion or power stations indicates formation of more and more chlorinated substances, when sampling in the direction from an exit from the combustion chamber to output section. From here, it is possible to draw a conclusion that the majority of dioxins is formed consistently with process of burning or in heat exchangers. The role of the combustion chamber consists in delivery of molecules - harbingers of formation of dioxins. Defining conditions for minimization of processes of formation of these harbingers, it is possible to limit to that and emission of dioxins [16-18].

Calculations showed in an assumption of chemical balance that thermodynamic barriers to disintegration of dioxins, furans, biphenyls at temperatures characteristic of burning of chemical fuels ($T > 1400$ K) do not exist. With sufficient residence time in the chemical reactor (combustion chamber) and excess oxygen, dioxins and any other organic compounds decompose, indicating the predominant influence of kinetic factors [19-21].

The models of processes of formation of harbingers of dioxins based on concepts of chemical thermodynamics and formal chemical kinetics and separate calculation results on the developed models and algorithms were considered.

2 Materials and methods

2.1 Disequilibrium Change of Decomposition Products

For the majority of units in which processes proceed at high temperature different disequilibrium effects are peculiar. The most important of them is the disequilibrium change of composition of combustion products, heating or decomposition caused by final speeds of the proceeding chemical reactions resulting in significant effect on the key power parameters of process [22].

These processes are described within formal chemical kinetics and consist in determination of structure of a working body on the set mechanism and constants of speeds of reactions. It is accepted that all transformations in a gas phase are elementary, i.e. proceed in one stage. Any chemical interactions can be provided by set of these elementary stages. In the work, the method of the solution of the equations of chemical kinetics described in a source was accepted [22-25].
Chemical reactions of three types are most probable: mono - bi- and three molecular. In a general view, the equation of chemical reaction is presented in the following form:

\[
\sum_{i=1}^{n} v_{ij} B_i \rightarrow \sum_{i=1}^{n} v'_{ij} B_i, j=1, \ldots, m, \tag{1}
\]

where \(B_i (i = 1, \ldots, n)\) – component (the reacting system consists from \(n\) - components between which proceed \(m\) reversible chemical reactions, that is proceeding as in direct, and in the opposite direction); \(v_{ij}, v'_{ij}\) – stoichiometric coefficients of \(j\) reaction.

The fundamental law of formal chemical kinetics is the law of the operating masses according to which the speed of change of maintenance of the \(i\) component on forward direction of the \(j\) reaction is a ratio:

\[
W_{ij}^+ = (v''_{ij} - v'_{ij}) k_j^+ \Pi_{k=1}^{n} c_k^v \tag{2}
\]

For backward direction:

\[
W_{ij}^- = (v'_{ij} - v''_{ij}) k_j^- \Pi_{k=1}^{n} c_k^v \tag{3}
\]

where \(k_j^+, k_j^-\) - constants of speed of \(j\) reaction in forward and backward direction.

In formal chemical kinetics of a constant of speeds of both direct, and reverse chemical reactions it is usually accepted to represent in the Arrhenius’s form.

For forward direction:

\[
k_j^+ = A_j^+ T^{n_j^+} \exp \left(-\frac{E_j^+}{R_0 T}\right) \tag{4}
\]

where \(R_0\) – universal gas constant, \(A_j^+, n_j^+, E_j^+\) – coefficients the \(j\) reactions characterizing forward direction (a pre- exponential factor, a temperature coefficient and activation energy respectively). The specified coefficients are defined empirically.

Constants of speed of forward and backward direction of reactions are connected through constants of balance of the last:

\[
K_{pj} = k_j^+/k_j^- \tag{5}
\]

Balance constant, being function of temperature, defines at the same time the relation of equilibrium values of concentration of the reacting components, i.e. concentration at which speeds of direct and reverse reaction are equal, i.e. \(W_{ij}^+ = W_{ij}^-\).

In this case:

\[
K_{pj} = \sum_k c_k^v k_j^+ / \sum_k c_k^v \tag{6}
\]

Constant of balance it is expedient to present combinations of the dissociation constants expressed through partial pressures in the form:

\[
K_{pj} = \frac{\Pi_{k=1}^{n} (k_k^P)^{v'ij}}{\Pi_{k=1}^{n} (k_k^P)^{v''ij}} R_0 T \sum_k (v''_{ij} - v'_{ij}) \tag{7}
\]

where \(K_k^D = \frac{\sum p_k}{\sum p_k^s}, a_{s,k} - \) stoichiometric coefficients in reaction of dissociation of substance to atoms.

In formal chemical kinetics, the principle of independence of course of elementary chemical reactions is provided in the reacting mixture. That is, the general speed of change of any component in mixture is equal to the algebraic sum of speeds of its change in result of course of all elementary reactions going at the fixed volume:

\[
\frac{dc_i}{dt} = W_i = \sum_{j=1}^{m} W_{ij}^+ + \sum_{j=1}^{m} W_{ij}^-, \tag{8}
\]

where \(i = 1, \ldots, n, j = 1, \ldots, m, n - \) number of individual substances; \(m - \) number of chemical reactions.

Using the formulas (2) and (3) the formula (8) can be written in the following way:

\[
\frac{dc_i}{dt} = \sum_{j=1}^{m} (v''_{ij} - v'_{ij}) k_j^+ \Pi_{k=1}^{n} c_k^v + \sum_{j=1}^{m} (v'_{ij} - v''_{ij}) k_j^- \Pi_{k=1}^{n} c_k^v \tag{9}
\]
2.2 Method of the Solution of the Equations of Chemical Kinetics

A reactive gas system is considered in which reversible elementary chemical reactions \( S = 1, \ldots, m \) occur between the components of the \( A_i (i = 1, \ldots, n) \), each reversible chemical reaction being considered as a set of two unilateral reactions. In advance, enter the following symbols:

\[
\begin{align*}
\nu_{ij} &= \nu_{i's} - \nu_{i's}, \quad n_{ij} = \nu_{i's}, \quad j = s, s = 1, \ldots, m; \\
\nu_{ij} &= \nu_{i's} - \nu_{i's}, \quad n_{ij} = \nu_{i's}, \quad j = s + 1, s = 1, \ldots, m.
\end{align*}
\]

(10)

According to the accepted designations the forward directions of chemical reactions have indexes \( j = 1, \ldots, m \), backward directions - indexes \( j = m + 1, \ldots, 2m \).

Applying a ratio \( C_i = n_i/V \) and \( r_i = n_i/V = C_i/C = p_i/p \) it is also possible to rewrite the equation (9) in the following form:

\[
\frac{1}{V} \frac{dn_i}{dt} = \sum_j \nu_{ij} k_j \left( \prod_p C_p^{n_{pj}} \right) C^{m_i},
\]

(11)

where \( i, p = 1, \ldots, n, \quad j = 1, \ldots, 2m, \quad C \) - mole concentration of gas mixture; \( C_p \) - mole partial concentration \( p \) component of gas mixture; \( m_i \) - sign of participation in \( j \) reaction of a catalytic particle \( M (m_j = 1) \), reaction proceeds with participation of this particle, opposite case \( m_j = 0; \quad n_i \) - number of moles of \( i \) component in volume \( V; \quad k \) - constant of speed of reversible chemical reactions.

Using ratios \( n_i = N r_i, \quad C_i = p r_i/R_0/T \), where \( N \) - total number of moths in volume \( V \), we will receive:

\[
\frac{1}{V} \frac{dn_i}{dt} = \frac{1}{V} \left( \frac{r_i dN}{dt} + N \frac{dr_i}{dt} \right) = \sum_j \nu_{ij} k_j \left( \frac{p}{R_0 T} \right)^{m_j} \prod_p \left( \frac{p}{R_0 T} \right)^{n_{pj}} r_p^{n_{pj}} = \sum_j \nu_{ij} k_j \left( \frac{p}{R_0 T} \right)^{m_j} \prod_p r_p^{n_{pj}},\]

(12)

The number of the equations (12) is equal to number a component of gas mixture. Summarizing \( i \) of all these equations, we will receive:

\[
\sum_i \frac{dN_i}{dt} + \sum_i N \frac{dr_i}{dt} = \sum_i \frac{dN_i}{dt} + \frac{N d(S \Sigma r_i)}{dt} = \Sigma_q \sum_j \nu_{ij} k_j \left( \frac{p}{R_0 T} \right)^{m_j} \sum_p r_p^{n_{pj}} \prod_p r_p^{n_{pj}},\]

(13)

where \( q = 1, \ldots, n \).

Having entered designation, \( \bar{m}_j = m_j + \Sigma n_{pj} - 1 \) and using equality \( N/V = p/R_0/T \) we will receive:

\[
\frac{dr_i}{dt} = \sum_j \nu_{ij} k_j \left( \frac{p}{R_0 T} \right)^{m_j} \prod_p r_p^{n_{pj}} - r_i \sum_q \sum_j \nu_{ij} k_j \left( \frac{p}{R_0 T} \right)^{m_j} \prod_p r_p^{n_{pj}},\]

(14)

where \( i, p, q = 1, \ldots, n, j = 1, \ldots, 2m \).

The ratio (14) is nonlinear differential equation which is integrated by means of numerical methods, and in this case for enough small concentration \( r_i \) of a rounding-off error can lead to obtaining physically unreal negative concentration \( r_i \). To prevent them, we will perform the following replacement \( \gamma_i = -\ln r_i \).

Then the equation of change of structure will take the following form:

\[
\frac{d\gamma_i}{dt} = -e^{\gamma_i} \sum_j \nu_{ij} k_j \left( \frac{p}{R_0 T} \right)^{m_j} \exp(-\sum_p n_{pj} \gamma_p) + \sum_q \sum_j \nu_{ij} k_j \left( \frac{p}{R_0 T} \right)^{m_j} \exp(-\sum_p n_{pj} \gamma_p),\]

(15)

where \( i, p, q = 1, \ldots, n, j = 1, \ldots, 2m \).

One of the equations (15) can be replaced with the normalization equation:

\[
\sum_i e^{-\gamma_i} = 1,\]

(16)

The equation, which describes change of the component, which is contained in gas mixture in the maximum concentration, is replaced.

Temperature change of a working body affects its thermodynamic and heat physical properties and on speeds of chemical reactions. Therefore, it is required to include a ratio, which connects structure of a working body with temperature in a mathematical model. It becomes based on a formula for a mixture enthalpy:

\[
i = \frac{\sum_i t_i r_i}{\sum_i r_i},\]

(17)
where \( l_i, \mu_i \) – values of a molar enthalpy and molecular mass of \( i \) component.

Values of a molar enthalpy, entropy and thermal capacity of individual substances of mixture is approximated by polynomials of IVTANTHERMO base, differing in the fact that operating range \( T=298.15...20000 \text{ K} \) is broken into six temperature ranges, each of which is described by polynomials with unique coefficients: \( \langle a_{-2}, a_{-1}, a_0, a_1, a_2, a_3 \rangle \):

\[
l_i(T) = \left[ H(T) - H(T_0) \right]_i + \Delta H_{f0i} \cdot 10^3,
\]

\[
H(T) - H(T_0) \equiv 10^4 \left[ -2a_{-2}x^{-1} + a_{-1} + a_1x + a_1x^2 + +2a_2x^3 + 3a_3x^4 \right],
\]

\[
S_i(T) = -a_{-2}x^{-2} + a_0 + a_l \ln x + a_l + 2a_1x + 3a_2x^2 + +4a_3x^3,
\]

\[
c_{pi} = -2a_{-2}x^{-2} + a_l + 2a_1x + 6a_2x^2 + 12a_3x^3,
\]

\[
x = T/1000.
\]

During performing calculations it is necessary to contact very often these ratios therefore for reduction of volume of calculations it is expedient to approximate them piecewise linear dependences of type:

\[
\hat{l}_i = l_i^{\text{basic}} + c_{pi}^{\text{basic}}(T - T_{\text{basic}}),
\]

where \( l_i^{\text{basic}} \) – basic value of a mole enthalpy of \( i \) component, \( T_{\text{basic}} \) – basic value of temperature; \( c_{pi}^{\text{basic}} \) – basic mole heat capacity equal to mean value on a linearization interval. With an accuracy, sufficient for the solution of applied tasks, this interval \( \Delta T \) it is possible to accept \( 100 \text{ K} \).

When using (18) the ratio (17) takes the following form:

\[
i = \frac{\sum [l_i^{\text{basic}} + c_{pi}^{\text{basic}}(T - T_{\text{basic}})] r_i}{\sum \mu_i r_i}.
\]

After simple transformations, we will receive:

\[
\frac{(T - T_{\text{basic}}) - \sum (l_i^{\mu_i} - l_i^{\text{basic}}) r_i}{\sum c_{pi}^{\text{basic}} r_i} = 0.
\]

The system of the equations used for determination of composition of high-energy chemical fuels includes the equations (15), (16), (20):

\[
\left\{ \begin{array}{l}
\frac{dy_i}{dx} = -e^{y_i} \sum_j v_{ki}k_j \left( \frac{p}{R_0T} \right)^m_j \exp(-\sum_p n_p y_p) + \\
+ \sum_q \sum_j v_{qj}k_j \left( \frac{p}{R_0T} \right)^m_j \exp(-\sum_p n_p y_p),
\end{array} \right. 
\]

\[
(y_i - T - T_{\text{basic}}) - \sum (l_i^{\mu_i} - l_i^{\text{basic}}) i / \sum c_{pi}^{\text{basic}} r_i = 0
\]

where \( i, p, q = 1, ..., n, j = 1, ..., 2m \).

Unknown in system (21) are the \( n \)-mole concentrations of the individual substances constituting the gas mixture and the temperature \( T \). For individual substances of components gas mixture and for all mixture in general ideal gas law is fair:

\[
pV = R_0T.
\]

The system (21) represents \((n - 1)\) the ordinary differential equations and one algebraic equation.

The specifics of the solution of a system (21) consist in "rigidity" of the equations of change of structure (15). Obtaining decisions for such equations is possible only when using implicit differential methods. An effective implicit method of final and differential approximation of the differential equations is the U.G. Pirumov’s method with the subsequent use of a method of Newton [22].

In order to use Newton’s method, differential equations must be pre-represented as the following uniform finite-difference equations:

\[
F_k^i \equiv X_{i,k-1}^n - X_i^n - h[a_i^S(\langle X_{ks}^n \rangle_i) + (1 - a) f_i^S(\langle X_{ks}^{n+1} \rangle_i)] \equiv 0,
\]

where \( i, k = 1, ..., q, q \) – number of unknown; \( h \) – integration step; \( a \) – approximation parameter \((a = 0.4); X_{k}^{n+1}; X_{ks}^{n+1} \) – values of unknown size at the beginning and the end of a step of integration.

The system (23) is nonlinear algebraic equations, which for the implementation of the Newton scheme can be converted to the form:

\[
\frac{dF_k^i}{dx_{ks}} \Delta X_{ks}^m = F_k^{ms},
\]

\[5\]
where $\left[ \frac{\partial F^l}{\partial X_{k}} \right]$ - matrix of private derivatives (Jacobi’s matrix).

The system of a look (24) is the system of already linear equations concerning amendments $\Delta X_{k}^n$, which can be solved by Gauss's method. The iterative scheme is applied to finding of unknown:

$$X_{i}^{n+1,m} = X_{i}^{n+1,m} + \Delta X_{i}^{n+1,m},$$

(25)

where $m$ – iteration number; $\Delta X_{i}^{n+1,m}$ – adjustments for $m$-th iteration; $(n + 1)$ – number of a step of integration on which the scheme is implemented; $i = 1, ..., q, q$ – number of unknown.

On a step of integration of iteration are executed before obtaining such values $X_{i}^{m}$, which differ from the previous values $X_{i}^{m-1}$ on predetermined small value.

The most time-consuming part of the algorithm is the calculation of the Jacobi matrix. The application of analytical calculation for it allows to keep "frozen" Jacobian on more steps of integration.

Special requirements are imposed on equations of composition change: they must be calculated in a generalized form. This will create a calculation program independent of the set of reactants and the set of chemical reactions.

For the system (21) reduced to of course difference form, the Jacobi matrix has the following elements:

$$\frac{dF_{i}}{d\gamma_{k}} = \delta_{i}^{k} + h (1 - a) e^{\gamma_{i}} \sum_{j} v_{ij} \Omega_{j} (\delta_{i}^{k} - n_{kj}) - \sum_{j} v_{pj} n_{kj} \Omega_{j},$$

(26)

$$\frac{dF_{i}}{d\gamma_{k}} = h (1 - a) e^{\gamma_{i}} \sum_{j} v_{ij} \Omega_{j} \left[ \frac{1}{\Omega_{j}} \frac{\partial A_{j}}{\partial T} + \frac{n_{j} - m_{j}}{T} + \sum_{j} (v_{pj} \Omega_{j} \left[ \frac{1}{\Omega_{j}} \frac{\partial A_{j}}{\partial T} + \frac{n_{j} - m_{j}}{T} \right] \right) - \sum_{j} v_{pj} n_{pj} \Omega_{j},$$

(27)

where $\delta_{i}^{k}$ – Kronecker's symbol; $\Omega_{j} = k_{j} \left( \frac{P}{R_{k} T} \right) \exp (- \sum_{p} n_{pj} \gamma_{p})$.

Calculation of constants of speeds of the reverse chemical reactions is provided in an algorithm of the Jacobi matrix. The application of analytical calculation for it allows to keep "frozen" Jacobian on more steps of integration.

Dissociation constants by the approximating coefficients are determined, which allow presenting dissociation constants in the form of the truncated dependence of Arrhenius’s type:

$$K_{D}^{i} = A_{D}^{i} \exp (-E_{D}^{i} / R_{k} T).$$

(29)

To reduce the calculation time, the entire operating temperature range 300...4200 $K$ is divided into equal temperature intervals with twenty "reference" points.

In these reference points for each individual substance, which is taking part in calculations in the corresponding array reference values of dissociation constants, are calculated and register previously:

$$\ln K_{i}^{D, basic} = \sum_{i} a_{im} s_{i}^{m} + \sum_{i} a_{im} i_{i}^{m} - s_{m} \sum_{i} a_{im} i_{i}^{m}. \tag{30}$$

where $a_{im}$ – number of atoms $i$ in a molecule of substance dissociation $m$.

Values of dissociation constants the approximating coefficients for definition of dissociation constants on the right and left borders of temperature intervals are calculated:

$$T_{+} = T_{basic} + 100 K, T_{-} = T_{basic} - 100 K, A_{+D}, A_{D}, E_{+D}, E_{D}. \tag{28}$$

2.3 Problem Statement. The Accepted Chemical Mechanism

The objective is to carry out a numerical experiment to predict the formation and decomposition of chlorine-containing hydrocarbons, which are precursors of dioxins in thermal power plants; Predicting concentrations of the resulting compounds; Determination of the range of temperatures and pressures that are characteristic of the maximum concentrations of the compounds in question.

In this experiment, the process of decomposition $C_{2}H_{5}Cl$ (chlorobenzene) was predicted.

Schemes of the models developed for carrying out numerical experiments are presented on figure 1. In the first experiment, the system of flowing non-stationary reactors of ideal mixing is considered. In
the first reactor methane is brought (methane with mass flow equal $\dot{m} = 0.1 \text{ kg/sec}$) + air (with mass flow $\dot{m} = 1.72 \text{ kg/sec}$), at stoichiometric ratio of components (coefficient of excess of oxidizer $\alpha = 1$), pressure in the reactor – 1 atm. On mass flows methane + air and time of stay of mixture in the reactor is timed $\tau = \frac{V\rho}{\dot{m}} = 5 ... 10 \text{ m/sec}$, what corresponds to reactor volume $V = 0.05 ... 0.1 \text{ m}^3$. We accept volume value $V = 0.08 \text{ m}^3$.

By integrating the resulting system of chemical kinetics equations in a given reactor, the chemically equilibrium composition of the mixture to be burned can be established.

In the second flowing reactor we reduce mixture temperature due to withdrawal of heat $Q$, kJ/sec:

- $3400 - T = 1000 \text{ K}$, $3200 - T = 1100 \text{ K}$, $3000 - T = 1200 \text{ K}$, $2800 - T = 1300 \text{ K}$, $2500 - T = 1400 \text{ K}$ to receive the temperature range of destructive conversions of chlorobenzene.

In the third flowing reactor chlorobenzene with different mass fractions moves: $g = 0.0001$ (0.01%); $g = 0.001$ (0.1%); $g = 0.1$ (10%) from total amount of mix.

In the fourth reactor, for chlorobenzene decomposition process consideration, the multicomponent structure is considered.

In the second experiment, the supply to group of flowing reactors of mixture of combustion products is made (methane+air at $\alpha = 1$) and the products of decomposition containing chlorine-containing connections (chlorobenzene $C_6H_5Cl$, tetrachloroethylene $C_2Cl_4$ etc.). In this case, the model structure of products of decomposition was accepted typical for model fuels.

### 3 Results and discussion

The results of the conducted computing researches on the first model are presented in figures 2-5.

At small values of a mass fraction of chlorobenzene and temperatures $\sim 1000 \text{ K}$ there is an insignificant decrease in concentration of chlorobenzene, and at a temperature $T > 1100 \text{ K}$ sharp falling at the initial moment of concentration of chlorobenzene, and then stabilization and even insignificant subsequent growth at $T > 1200 \text{ K}$ (figure 2).
Figure 2. Change of a mole dole of chlorobenzene at a mass fraction \( g = 0.0001 \) from composition of mixture and various reference temperatures:

1 – 1000 \( K \); 2 – 1100 \( K \); 3 – 1200 \( K \); 4 – 1300 \( K \); 5 – 1400 \( K \).

At a temperature, \( \sim 1000 \) \( K \) at a mass fraction of chlorobenzene of equal there is a rectilinear falling of concentration of chlorobenzene (figure 3). But at temperatures \( \sim 1100 \ldots 1300 \) \( K \) to decrease sharply in concentration, with the subsequent smooth alignment on 0.5 sec. and further. At a temperature \( \sim 1400 \) \( K \) there is a sharp decrease in concentration during the completely considered time.

Figure 3. Change of a mole dole of chlorobenzene at a mass fraction \( g = 0.001 \) from composition of mixture and various reference temperatures:

1 – 1000 \( K \); 2 – 1100 \( K \); 3 – 1200 \( K \); 4 – 1300 \( K \); 5 – 1400 \( K \).

When reference temperature is equal \( 1000 \) \( K \) the character of change of a curve is rectilinear. At \( T \geq 1300 \) \( K \) at first concentration of chlorobenzene sharply falls, and then monotonously decreases on time. At a mass fraction of chlorobenzene \( g = 0.1 \) its concentration at temperatures \( T \leq 1100 \) \( K \) grows, and at \( T \geq 1200 \) \( K \) at the initial moment grows, and then in time \( t > 0.01 \) sec. falls (figure 4).
Figure 4. Change of a mole dole of chlorobenzene at a mass fraction $g = 0.1$ from composition of mixture and various reference temperatures:

1 – $1000 \, K$; 2 – $1100 \, K$; 3 – $1200 \, K$; 4 – $1300 \, K$; 5 – $1400 \, K$.

Figure 5. Change of mole dole of chlorobenzene depending on temperature and a mass fraction of the brought decomposition products:

1 – $g = 0.03$; 2 – $g = 0.04$; 3 – $g = 0.05$.

The results of the second computing experiment, which show changes of molar concentration of chlorine-containing connections depending on temperature and a mass fraction of products of decomposition of high-energy chemical fuels, are given in figure 5. The received results meet physical expectations of conversion of chemical fuels and the gas-phase mechanism of chemical reactions accepted in calculation. Concentration chlorobenzene on temperature have peak in the range from $1000 \ldots 1300 \, K$ and sharp decrease in a molar share at more high temperature (figure 5) which is defined by the used mechanism of chemical reactions.
Figure 6. Change of mole dole of tetrachloroethylene depending on temperature and a mass fraction of the brought decomposition products: $1 - g = 0.03; 2 - g = 0.04; 3 - g = 0.05$.

Figure 7. Change of mole dole of molecular chlorine depending on temperature and a mass fraction of the brought decomposition products: $1 - g = 0.03; 2 - g = 0.04; 3 - g = 0.05$.

Change of concentration $C_2Cl_4$ (figure 6) is typical, with temperature increase it sharply decreases. Change of other concentration of connections with chlorine $Cl_2$ is shown in figure 7. Concentration of chlorine $Cl_2$ has a minimum at a temperature $1000 \, K$ and increases with of temperature growth.

Taking into account the made numerical experiments the following recommendations for minimization of emission of dioxins when burning chemical fuels are made:

1. It is offered to carry out the technological process based on a thermochemical method of conversion of complex chemicals and their mixtures at high temperatures (~2500…3000 $K$) with the subsequent sharp decrease in temperature to values $T < 450 \, K$, causing "freezing" of high-temperature products of reactions. In a high-temperature zone dioxins are not formed. In a low-temperature zone, the formation of secondary dioxins is complicated because of low speeds of chemical reactions. Sharp decrease in temperature can be carried out or expansion of combustion.
products in nozzles to the speeds coming to sound or introduction to high-temperature products of reactions of water or salt solutions.

2. It is offered to carry out the improvement of the organization of process of burning leading to the fullest combustion and, therefore, reduction of concentration of organic molecules and sooty particles. Without availability of organic substances at temperatures of 500…800 K dioxins are not formed. Reduction of their output will promote decrease in emission of dioxins.

3. It is offered to study mechanisms of formation of dioxins. It will allow developing a number of the approaches directed to improvement of modern methods of combustion of chemical fuels for the purpose of reduction of an output of dioxins.

4. Alternative method is adding additives to off gases, which inhibit the superficial reactions responsible for formation of dioxins.

4 Conclusions
Based on the analysis of the available data on mechanisms of speeds of chemical reactions of transformations of chlorine-containing connections the possible kinetic models of processes in combustion chambers allowing describing qualitatively dynamics of decomposition of harbingers of the dioxins, which is a part of products of burning of chemical fuels, are formed.

Possible ways of minimization of emission of dioxins at combustion of chemical fuels are represented.

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