Macrokinetics of laser-induced chemical reactions in gases

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This paper deals with the problem of laser radiation interaction with chemical gas. The review of numerical simulation results on the basis of three different models is presented. The main modes of the system behavior and the conditions, with various processes (diffusion, thermoconductivity, thermal diffusion, heat effect of the reaction and others) contributing to their realization, have been established. Theorems about the convergence of finite difference schemes have been proved.

1. Introduction

As it is well known, the interaction of an optical radiation with chemically active gas media has attracted the attention of scientists for many years (see, for instance, refs. [1–6]). This is accompanied with theoretical interest in this phenomenon and numerous possible applications of such results. For instance, laser beams can be used for control of the chemical reaction rate at chemical enterprises, for activation of chemical reactions, in the systems of the air control around big cities, systems of optical communications and so on. Besides, the "beam–substance" systems are very interesting from the theory of self-organizing point of view because of a great number of nonlinear processes. As far as the effect of the optical radiation on a chemically active gas is concerned, it has been shown by other authors [3] that the dependence of the reaction product yield on the intensity of the radiation incident on a thin nonlinear medium layer may have a bistable character. It means that the system has two steady states, and their realization depends only on the initial state and external influences. The present paper is a review of our studies and results, which were originally published in refs. [7–18].

Two points should be emphasized. Firstly, the problem has a long history and in this paper we shall make a general review of our models, numerical methods and nonlinear effects in gas media. We suppose that the compilation of these results in one paper will be interesting for the researcher of laser thermochemistry and nonlinear dynamical systems, because articles in Soviet scientific journals are inaccessible to a great number of foreign scientists. Besides, as far as we know, all of the

models and results which are included in this paper were not investigated before but now some of them have been obtained by experiment. Unfortunately for the most part these are unpublished results of other scientific groups and we may not discuss them in our article. Secondly, we shall not discuss the results of other scientists since that would make the present paper too lengthy for a journal.

In section 2 three mathematical models describing the laser beam interaction with a chemically active gas are represented. Note that we studied only bimolecular and monomolecular chemical reactions because more complicated reactions consist of a great number of stages, each of them being either bimolecular or monomolecular. Therefore investigation of laser beam influence on multistage chemical reactions is impossible without an understanding of the nonlinear processes in the case of bimolecular chemical reactions. Besides, if the concentration of one of the initial substances is sufficiently greater than that of another one, we may investigate this reaction as a monomolecular one by supposing that this substance is a buffer gas and the constant of direct reaction, depending on the buffer gas concentration, does not change during the time of laser influence.

The next three sections contain the results of mathematical modelling using corresponding models. In section 3.1 we briefly describe optical bistability in the case of a "point" model (optically thin medium without diffusion, thermal diffusion and so on). As a result of this bistability, different types of chemical reaction localization in the case of inhomogeneous laser radiation are obtained and studied at the end of section 3.2 and sections 4.2, 5.1 and 5.3. In these sections we investigate the influence of diffusion, heat effect of the chemical reaction, and thermal diffusion (section 5.3) on this localization. For the first time it has been shown (section 5.3) that under some conditions the heat effect of the chemical reaction can increase the inhomogeneities of gas components and temperature distributions. At the end of section 4.2 we study the stabilization of the time profile of the laser beam as a result of optical bistability in the medium.

Different oscillations are investigated in sections 3.2, 3.3 and 4.1 and at the end of section 5.3. In sections 3.2 and 4.1 we describe the moving "hump" of concentration as a result of the difference between the rates of chemical reaction and heating of the medium. In section 3.3 we investigate the case of strong dependence of the absorption coefficient on temperature. Some conditions for the existence of relaxational oscillations have been obtained. Oscillations discussed in section 5.3 are the result of thermal diffusion of components. Some other stationary thermal diffusion structures are investigated in section 5.2.

In section 6 we briefly describe numerical methods that we have used for computing.

2. Problem formulation and basic equations

Consider a cylindrical vessel (l – vessel length, R_v – radius) with a surface

through which the heat exchange with the external medium occurs. The vessel is filled with a gas mixture in which a reaction A $\rightleftarrows$ C or A+B $\rightleftarrows$ C proceeds. We suppose that the cylinder's walls are impermeable. The light pulse is incident on its end surface (fig. 1). We investigate three main models of the heat influence of laser radiation over the chemically active gas. We consider both an optically thin and an optically thick layer without due regard for convection. All equations are written in a dimensionless form. Therefore one set of dimensionless parameters gives rise to a large number of different sets of physical variables.

The conditions under which the convection in our system may be negligible have been obtained by the authors of ref. [5]. In particular, it is necessary that the pulse duration must be considerably longer than the time of the $V-T$ relaxation (τ_{VT}). Here τ_{VT} is the relaxation time for the molecular vibrational energy to be transferred to a translational degree of freedom.

(a) $l \gg R_v$, $R_v < R_i$ ($R_i - beam\ radius$), A+B $\rightleftarrows$ C

$$\frac{\partial N_C}{\partial t} = f + D_C \frac{\partial^2 N_C}{\partial z^2} \,,$$

$$\frac{\partial N_{A,B}}{\partial t} = -f + D_{A,B} \frac{\partial^2 N_{A,B}}{\partial z^2} \,, \quad 0 < t \leqslant t_0 \,, \quad 0 < z < 1 \,,$$

$$\epsilon \frac{\partial T}{\partial t} = qI(\delta_A N_A + \delta_B N_B + \delta_C N_C) + D_T \frac{\partial^2 T}{\partial z^2} + \gamma f - (T - T_{\text{out}}) \,,$$

$$\frac{\partial I}{\partial z} + \delta I(\delta_A N_A + \delta_B N_B + \delta_C N_C) = 0 \,,$$

$$f(N_A, N_B, N_C, T) = N_A N_B \exp(-1/T) - k N_C \exp(-T_C/T) \,, \tag{1}$$

with the following boundary and initial conditions:

$$\left. \frac{\partial N_{A,B,C}}{\partial z} \right|_{z=0,1} = 0 \,, \quad \left. \frac{\partial T}{\partial z} \right|_{z=0,1} = 0 \,,$$

$$N_A(0, z) = 1 \,, \quad N_C(0, z) = N_{C0} \,, \quad N_B(0, z) = N_{B0} \,, \quad T(0, z) = T_{\text{out}} \,. \tag{2}$$

Here $N_{A,B,C}$ are the concentrations of the gas components A, B and C, respec-
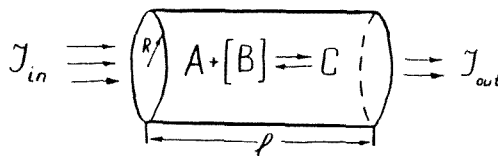

Fig. 1.

tively. $N_{A,B,C}$ are normalized with respect to the total number of molecules of the gas component A, T is the mixture temperature measured in terms of the activation energy of the forward reaction, T_C is the ratio of the activation energies of forward and reverse reactions, $D_{A,B,C,T}$ characterize the diffusion coefficients of the substance and thermoconductivity $t = t'k_A$, here t' is time, $k = k_C/k_A$, k_A and k_C are the rate constants of the direct and reverse reactions, ϵ is the ratio of the rate of the mixture temperature variation, caused by the heat exchange, to the forward reaction rate with due regard for the medium specific heat and the medium density. $T - T_{out}$ describes the heat exchange with the ambient reaction zone medium, which has the temperature T_{out}. The sign of γ is determined by the difference between the activation energies of the reverse and forward reactions (in our notation it is characterized by the value of the parameter T_C: sign $\gamma =$ sign($T_C - 1$)). Note that we analyze the case when the reaction zone is sufficiently thin in the direction perpendicular to the coordinate z. And therefore the heat diffusion in these directions is treated by us with the help of the "Newtonian cooling" term in (1). This approach is widely used in the literature (see, for example, refs. [19,20]) when the optical bistability in a semiconductor is investigated. Thus the heat exchange depends on the radius of the vessel and that of the initial beam. The coefficient q characterizes the laser power, $\delta_{A,B,C}$ is the absorption coefficient of the components, δ is its amplitude value, z is the coordinate normalized with respect to the vessel length. Besides, for a great number of gases the diffusion along z may be negligible in the first stage of the research [8,10].

Concluding this section, we would like to remark that the results which are obtained in this model will be valid in the case of the reaction A $\rightleftarrows$ C. But in our case the optical bistability is realized for a much wider set of parameters values than in the case of the two component gas mixture.

(b) $l \gg R_v$, $R_v > R_i$, A+B $\rightleftarrows$ C

In this case we must take into account the diffusion of temperature and components A, B, C by the transverse coordinate r. Therefore we obtain the following system of dimensionless equations:

$$\frac{\partial N_C}{\partial t} = f + D_C \Delta_\perp N_C \,,$$

$$\frac{\partial N_{A,B}}{\partial t} = -f + D_{A,B} \Delta_\perp N_{A,B} \,, \quad 0 < t \leqslant t_0 \,, \quad 0 < r < R \,, \quad 0 < z < 1 \,,$$

$$\epsilon \frac{\partial T}{\partial t} = qI(\delta_A N_A + \delta_B N_B + \delta_C N_C) + \Delta_\perp T + \gamma f \,,$$

$$\frac{\partial I}{\partial z} + \delta I(\delta_A N_A + \delta_B N_B + \delta_C N_C) = 0 \,,$$

$$f(N_A, N_B, N_C, T) = N_A N_B \exp(-1/T) - k N_C \exp(-T_C/T),\qquad (3)$$

with the following boundary and initial conditions:

$$\left.\frac{\partial N_{A,B,C}}{\partial r}\right|_{r=0,R} = 0,\quad \left.\frac{\partial T}{\partial r}\right|_{r=0} = 0,\quad \left.\frac{\partial T}{\partial r}\right|_{r=R} = -\eta_b(T - T_{out}),$$

$$N_A(0, z, r) = 1,\quad N_B(0, z, r) = N_{B0},\quad N_C(0, z, r) = N_{C0},$$

$$T(0, z, r) = T_{out},\quad I(t, 0, r) = \phi(t)\psi(r).\qquad (4)$$

Here η_b is the heat exchange through the boundary surface of the vessel, $\Delta_\perp = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right)$, $D_{A,B,C}$ are the ratios of the diffusion coefficients of the components and $k_A a^2$, a is the initial radius of the beam, r is the transverse coordinate normalized with respect to a. $\psi(r)$ is the spatial profile of the intensity, which, for a Gaussian beam, is given in the form

$$\psi(r) = \exp(-r^2).$$

(c) $l \ll R_v$, $R_v > R_i$, $A \rightleftarrows C$

In this case we use an approximation in which the medium is considered to be thin, i.e. an approximation when all the processes in any cross section of the vessel proceed equally. As has already been noted, such an approach is widely used in practice. In this case, the effect of a light beam on a chemically active mixture with active diffusion and thermal diffusion is described by the following set of dimensionless differential equations:

$$\frac{\partial N_C}{\partial t} = f + D_C\Delta_\perp N_C + \alpha \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{N_A N_C}{T}\frac{\partial T}{\partial r}\right),$$

$$\frac{\partial N_A}{\partial t} = -f + D_A\Delta_\perp N_A - \alpha \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{N_A N_C}{T}\frac{\partial T}{\partial r}\right),\quad 0 < t \leqslant t_0,\quad 0 < r < R,$$

$$\epsilon\frac{\partial T}{\partial t} = qI(\delta_A N_A + \delta_C N_C) + \Delta_\perp T + \gamma f - \eta_e(T - T_{out}),$$

$$f(N_A, N_C, T) = N_A \exp(-1/T) - k N_C \exp(-T_C/T),\qquad (5)$$

with the following boundary and initial conditions:

$$\left.\frac{\partial N_{A,C}}{\partial r}\right|_{r=0,R} = 0,\quad \left.\frac{\partial T}{\partial r}\right|_{r=0,R} = 0,$$

$$N_A(0, r) = 1,\quad N_C(0, r) = N_{C0},\quad T(0, r) = T_{out}.\qquad (6)$$

Here α characterizes the thermal diffusion of components, η_e is the heat exchange with the ambient medium through the top and bottom surfaces.

3. Optically thick nonlinear medium without diffusion along the transverse coordinate (1), (2) [8,10,13]

In the beginning of this section we shall briefly describe the classical optical bistability for a "point" chemically active gas.

3.1. BISTABILITY IN THE CASE OF "POINT" MEDIUM

In this case, the temperature and concentrations of gases are the same everywhere in the vessel, and we can study the system of ordinary differential equations.

$$\frac{\partial N_C}{\partial t} = f, \quad \frac{\partial N_{A,B}}{\partial t} = -f,$$

$$\epsilon \frac{\partial T}{\partial t} = qI(\delta_A N_A + \delta_B N_B + \delta_C N_C) + \gamma f - (T - T_{out}), \quad 0 \leqslant t \leqslant t_0,$$

$$f(N_A, N_B, N_C, T) = N_A N_B \exp(-1/T) - kN_C \exp(-T_C/T),$$

$$I = \phi(t).$$ (7)

It can be shown that (7) is equivalent to

$$\frac{\partial N_C}{\partial t} = (1 - N_C)(N_{B0} - N_C) \exp(-1/T) - kN_C \exp(-T_C/T),$$

$$\epsilon \frac{\partial T}{\partial t} = qI(\delta_A(1 - N_C) + \delta_B(N_{B0} - N_C) + \delta_C N_C) + \gamma \frac{\partial N_C}{\partial t} - (T - T_{out}),$$

$$I = \phi(t), \quad 0 \leqslant t \leqslant t_0.$$

The authors of [3] showed that in the steady state system (7) can have a bistable dependence of N_C and T on $\phi(t = \infty)$. This dependence is shown in fig. 2 for: $N_{B0} = k = \delta_C = 1$, $T_{out} = 0.125$, $N_{C0} = \delta_{A,B} = 0$, $T_C = 0.375$ and $q = 5$. The system $\partial N_C/\partial t = \partial T/\partial t = 0$ has three solutions when $\phi(t = \infty) \in (1.6; 1.8)$, but only two of them are stable (1 and 3). Therefore the realization of one of these steady states depends on the initial conditions and external influence.

3.2. MEDIUM WITH CONSTANT ABSORPTION COEFFICIENTS ($\delta_{A,B,C} = $ Const) [10]

In this section we will describe our results for the model (1), (2) in the case of con-
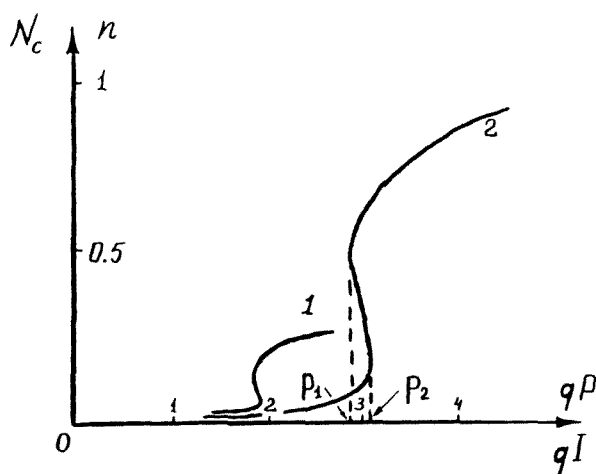
Fig. 2. Bistability in the case of "point" model (dependence of N_C on qI) – curve 1; bistability in the case of active diffusion (dependence of $n = \int_0^R rN_C dr$ on $qP = q\int_0^R rIdr$) – curve 2.

stant absorption coefficients. For such coefficients the kinetics of the chemical system is of two different types. For the first one $T_C > 1$ and we can observe a moving "hump" of N_C.

From the numerous experiments carried out for a wide range of parameters, it may be concluded that the maximum and stationary concentration values of the reaction product do not coincide somewhere in the medium or in the vessel as a whole. The different times taken to reach the product concentration maximum at the various points of the vessel result in the propagation of the product concentration "hump".

The dependence of N_C for $N_{A0} = \delta_C = 1$, $N_{C0} = \delta_{A,B} = 0$, $T_C = 3$, $q = 6.6$, $\gamma = 0$, $\epsilon = 0.1$ and $T_{out} = 0.33$ is illustrated in fig. 3(a). The formation of "hump" in the product concentration and its propagation over the volume of the medium can be seen in the figure.

Initially the concentration of the product increases for $z = 0$. This leads to an increase in the light energy absorption and to a rise in temperature; as a result the nonequilibrium value of the concentration increases too. Then the concentration of the product in this place decreases because the equilibrium value of N_C decreases with a rise in T, and the wave moves forward. Accordingly, the presence of a delay between changes in the temperature and concentration of the reaction product, as well as the existence of a further nonequilibrium state of the system, are important in this connection. It should be noted that the speed of the wave decreases along z.

In the case of optical bistability $(T_C < 1)$ the chemical kinetics becomes quite different. As a result of the bistability, the chemical reaction can be efficient only in a region $z < z_k$. In the region $z > z_k$ the N_C value is ten times less than in the first one. The temperature has the same dependence on z. This is illustrated in fig. 3(b) for
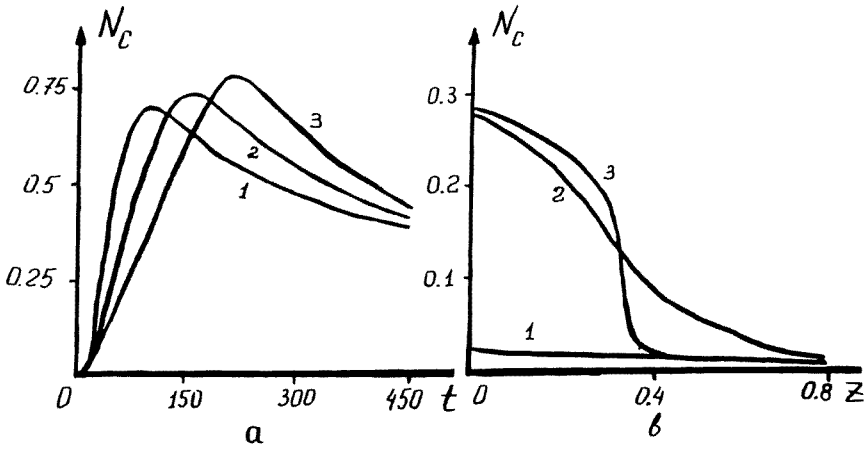
Fig. 3. (a) The "hump" of N_C in the case of $T_C > 1 : z = 0$ (1), 0.3 (2), 1 (3). (b) Localization of N_C in the case of $T_C < 1 : t = 50$ (1), 100 (2), 400 (3).

the following parameters: $N_{A0} = N_{B0} = \delta_C = 1$, $N_{C0} = \delta_{A,B} = 0$, $T_C = 0.375$, $q = 3.125$, $\gamma = 0$, $\epsilon = 2.5$, $T_{out} = 0.125$ and $\delta = 8$. This effect will be described in detail for the case of efficient diffusion.

3.3. THE CASE $\delta_{A,B} = 0$, $\delta_C(T) = \exp(-T_H/T)$ [8,13,21]

3.3.1. The case of thin nonlinear medium layer (system (7))

In this section we shall analyze briefly the conditions under which oscillations of the gas components and temperature take place. For the sake of simplicity, we first consider the case $\gamma = 0$ (but $T_C > 1$). Using the standard technique for the analysis of an ordinary differential equation system [22,23] we shall study following linear system of ordinary differential equations:

$$\frac{\partial \tilde{N}_C}{\partial t} = (1 - N_*)^2 \exp(-1/T_*) \frac{\tilde{T}}{T_*^2} - (2(1 - N_*) \exp(-1/T_*)$$

$$+ k \exp(-T_C/T_*)) \tilde{N}_C - k N_* \exp(-T_C/T_*) \frac{\tilde{T}}{T_*^2} T_C,$$

$$\epsilon \frac{\partial \tilde{T}}{\partial t} = q \tilde{N} \exp(-T_H/T_*) + q N_* \exp(-T_H/T_*) \frac{\tilde{T}}{T_*^2} T_H - \tilde{T}. \tag{8}$$

Here N_*, T_* are the solution of the system:

$$\frac{\partial N_C}{\partial t} = (1 - N_C)(N_{B0} - N_C) \exp(-1/T) - k N_C \exp(-T_C/T) = 0,$$

$$\epsilon \frac{\partial T}{\partial t} = q \phi(t = \infty) \delta_C(T) N_C + \gamma \frac{\partial N_C}{\partial t} - (T - T_{out}) = 0. \tag{9}$$

We readily obtain the following condition which is necessary for the realization of the temperature oscillations:

$$\delta_C(T) - (T - T_{out})\frac{\partial \delta_C(T)}{\partial T} < 0 \qquad (10)$$

because the dependence of N_C on T obtained from the equation $\partial N_C/\partial t = 0$ is a monotonic one. Inequality (10) defines the interval of the temperature values (T_1, T_2). If the condition (10) is valid, then system (9) can have more than one steady solution. The case when the system $\partial N_C/\partial t = 0$, $\partial T/\partial t = 0$, has only one solution is of particular interest to us. Note that T_* needs also to belong to the interval (T_1, T_2) of temperature values, which in our case is equal to $(0.3, 0.7)$.

The value of ϵ is of great significance for the realization of temperature oscillations. If $\epsilon \ll 1$ (in this case the temperature changes faster than the concentration) then N_C and T are in the vicinity of the curve $\partial T/\partial t = 0$ for the most part of time (see, for instance, fig. 4). Note, that the temperature and concentration change slowly on the curve part a, c and they change rapidly on the curve part b, d. The rate of motion along the curve parts a, c and b, d is defined by the parameters of the
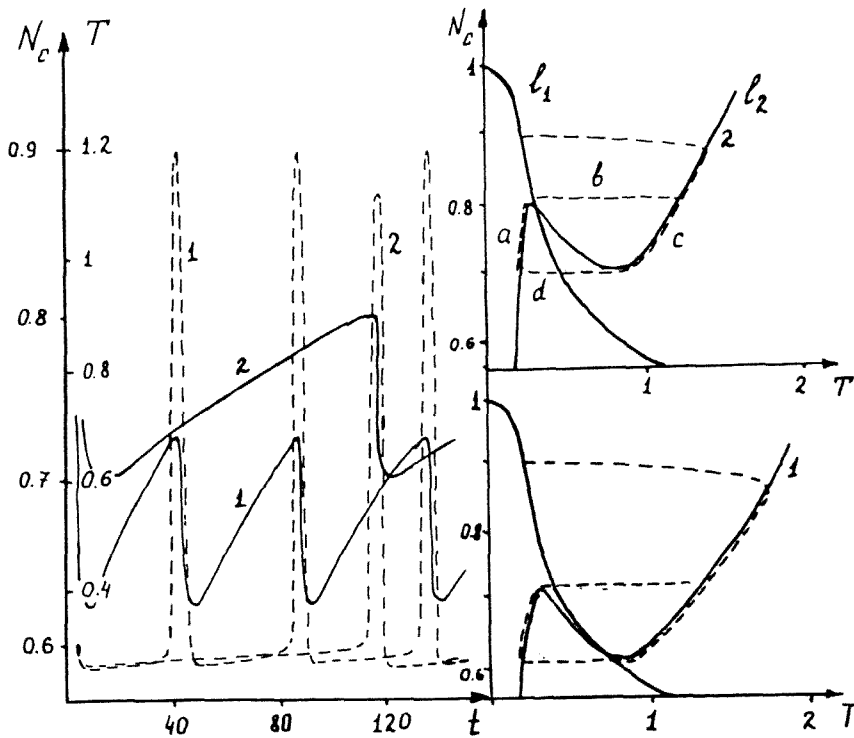

Fig. 4. Oscillations of N_C (solid lines) and T (dashed lines) for $q = 3.12$ (curves 1), 2.84 (curves 2) and trajectories on the plane $\{N_C, T\}$ for $q = 3.12$ (1) and 2.84 (2). Here $l_1 : \partial N_C/\partial t = 0$, $l_2 : \partial T/\partial t = 0$.

equations for N_C and T, respectively. To define the maximum $\epsilon(\epsilon_{cr})$ for which the temperature oscillations vanish we have to obtain from the system of equations (9) the linear one around the point (N_*, T_*) (see (8)). We get after some algebra

$$\epsilon_{cr} = \frac{qN_* \exp(-T_H/T_*)T_H T_*^{-2} - 1}{2(1 - N_*) \exp(-1/T_*) + k \exp(-T_C/T_*)} . \tag{11}$$

It is essential that N_*, T_* are the solution of the transcendental equations $\partial N_C/\partial t = 0$, $\partial T/\partial t = 0$, and depend on the parameters q, T_{out}, T_C, k and T_H. Therefore the obvious dependence of ϵ_{cr} on these parameters is absent. However, notice that the oscillations are possible if q belongs to the interval (q_1, q_2) which is defined by the following inequality:

$$qN_* \exp(-T_H/T_*)T_H - T_*^2 > 0 \tag{12}$$

(see expression (11)). Generally, the temperature values T_1, T_2 define the concentration values N_1, N_2 and correspondingly define the intensity power values q_1, q_2:

$$q_{1,2} = \frac{T_{1,2} - T_{out}}{N_{1,2} \exp(-T_H/T_{1,2})} . \tag{13}$$

To conclude this section we shall consider the influence of the thermal effect of a chemical reaction. By carrying out an analogous linearization we obtain the following expression for the maximum $\gamma(\gamma_{cr})$ at which the temperature oscillations vanish:

$$\gamma_{cr} = \frac{qN_* \exp(-T_H/T_*)T_H - T_*^2}{(1 - T_C)k \exp(-T_C/T_*)N_*} . \tag{14}$$

3.3.2. The case of thick nonlinear medium layer

In this section we shall analyze the propagation of a light pulse in the vessel. Consider the case of $\gamma = 0$, $D_{A,B,C,T} = 0$, when the temperature and concentration oscillations exist (if $\epsilon < \epsilon_{cr}$). The influence of diffusion on the oscillations is not analyzed in this article. Notice that the coefficients $D_{A,B,C,T}$ and γ can be changed by means of a change in the buffer gas density, the vessel radius and length. Therefore their values can be diminished.

Figure 5 shows the results obtained with the help of the numerical solution for the following equation parameters: $T_C = 2$, $T_H = 1$, $k = 1$, $\delta = 8$, $\epsilon = 0.01$, $q = 5$. In this case the pulse intensity is greater than $q_{1,2}$. As it follows from fig. 5, there are three areas of temperature and concentration changes. In the first area $(0 \leqslant z \leqslant z_1)$ where qI is more than q_2 the temperature (the concentration) is monotonically decreasing (increasing) when the coordinate z increases. In the second area $(z_1 \leqslant z \leqslant z_2$, correspondingly $q_2 > qI > 1_1)$ the temperature and the concentration waves exist and move along z. Then in the third area the temperature varies slowly
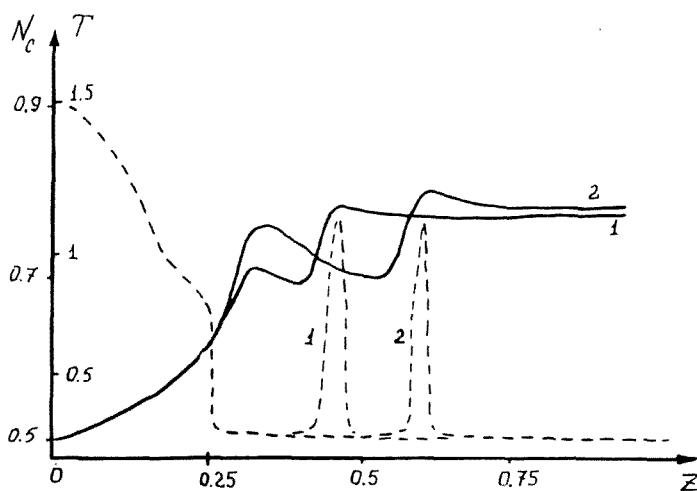
Fig. 5. Moving structure in the optically thick case: $t = 66$ (1), 95 (2).

along the coordinate z, but the concentration waves propagate also in this case. Note that the area (z_1, z_2) depends on the light power and the absorption coefficient in particular. The thermal effect of the reaction (if $\gamma < \gamma_{cr}$) and diffusion (if it is small enough) change the temperature and concentration amplitudes but the waves exist.

4. Optically thick nonlinear medium with efficient diffusion of temperature and components [7,11,16]

In contrast to a system without diffusion, in this case the dynamics of the chemical reaction is determined not only by the energy release constant (γ), the initial power of the beam and the rate of heat exchange with the surroundings, but also by the rates of diffusion of heat (thermoconductivity) and the components of the gas mixture.

Let the parameters of the process be such that the diffusion of gas components does not have any substantial influence on the chemical reaction. Then, at the beginning of the laser action, for $t < t_T$ (where t_T is the characteristic heat redistribution time due to its diffusion) the kinetics of the chemical reaction and propagation of the pulse proceed as in the previous case. After the end of this time interval the further course of the process will depend on the ratio of the rates of heating and heat exchange as well as on the temperature of the surroundings. We shall assume that an S-like dependence of the product concentration on the light beam intensity is possible. Then, if the outflow of heat due to its diffusion exceeds the heating,

the initially occurring concentration localization over the transverse coordinate will flatten out. In the opposite case the localization will be constant and stable.

if the diffusion of gases is substantial, then three situations may arise. For example, in the case when the medium heats up more quickly than any one of the components (for example, the reaction product) diffuse, a sharp change in its concentration may be established. In the opposite situation the transverse profile of the component concentration repeats the beam profile. Under a rough equality of the rates of the component diffusion and temperature of the medium, the concentration wave of this component propagates to the lateral boundary of the cylinder. It is important to emphasize that all these situations are possible for different components of gas simultaneously. Accordingly, it is necessary to observe the localization of a chemical reaction on one of the components of the gas mixture.

4.1. THE $T_C > 1$ CASE

4.1.1. Numerical simulation [7,11]

From the numerous numerical experiments carried out with a wide range of parameters follows that in general the kinetics of reaction repeats the case 3.2. But the "hump" of the product propagates along r and z. The dependences N_C in the case of a three-component mixture for $\eta_b = 1$, $T_C = 1.375$, $q = 133$ and $D_{A,B,C} = 0.002$ are illustrated in fig. 6.

It is significant that in the absence of diffusion (short pulses) the formation of the "hump" along the transverse coordinate was not observed. The parameters of the "hump" depend on the ratio of diffusion coefficients. Thus, if $D_C < D_{A,B}$ (for example, $D_C = 0.01$ and $D_{A,B} = 0.1$), the concentration wave becomes more sharply expressed: the maximum value of N_C increases by a factor of 1.2 compared with
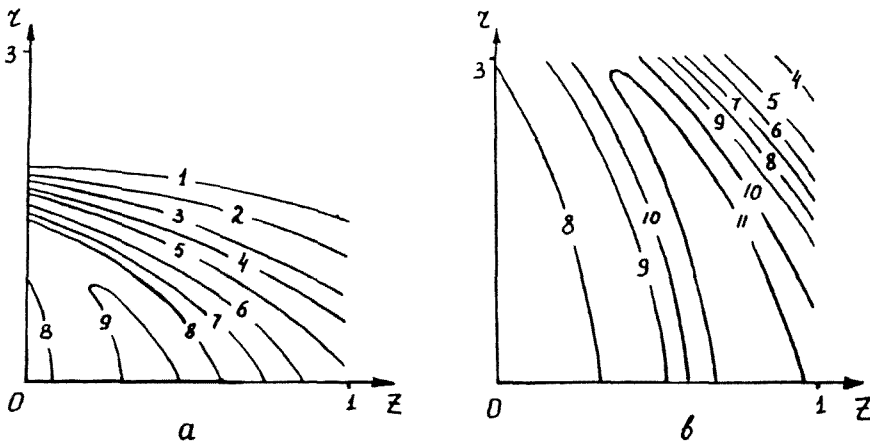

Fig. 6. Space distribution of N_C for $t = 50$ (a), 200 (b). Here $N_C = 0.05$ (1), 0.1 (2), 0.15 (3), 0.2 (4), 0.25 (5), 0.3 (6), 0.35 (7), 0.4 (8), 0.45 (9), 0.5 (10), 0.55 (11).

the case $D_C = D_{A,B}$. This is associated with the fact that substance C diffuses from the reaction zone more slowly than the initial substances inflow to this zone.

For $D_C > D_{A,B}$ (for example, $D_C = 0.1$), the change in the product concentration exhibits an oscillating behaviour (1–4% of the average value). However, for this to occur the initial intensity of the beam should exceed some critical value.

The heat effect of the reaction ($\gamma = 3.3$) leads to stabilization of N_C for $z > 0.72$. At the beginning of the volume the concentration of the product decreases by a factor of 1.72 on the axis, and for $r = R$ by a factor of 1.4. It is important to emphasize that the formation of the concentration "hump" disappears with an increase in γ.

In conclusion we would like to remark that under the action of optical radiation on a chemically active gaseous mixture, a process with an explosive-like absorption may occur. This is illustrated in fig. 7, where in particular three phases of the process are clearly visible: practically complete absence of absorption, rapid growth of absorbtion and a stationary level.

4.1.2. Analytical study of explosive-like absorption [16]

As it was shown in the previous section, the system kinetics has three phases in the case of explosive-like absorption. From the practical point of view, it is interesting to study the dependence of the first period length on the main system parameters.

From the numerical simulation carried out, the following conditions of such absorption may be concluded: $(\delta_C/(\delta_A + \delta_B)) \gg 1$, $T_C > 1$, $N_{C0} \ll N_{A0,B0}$. Besides, the exponential dependence of the chemical reaction rate on temperature leads to an explosive increase in N_C and light absorption when $T \cong 0.4$. That is why we may approximate (3), (4) by the following linear system of ordinary differential equations:
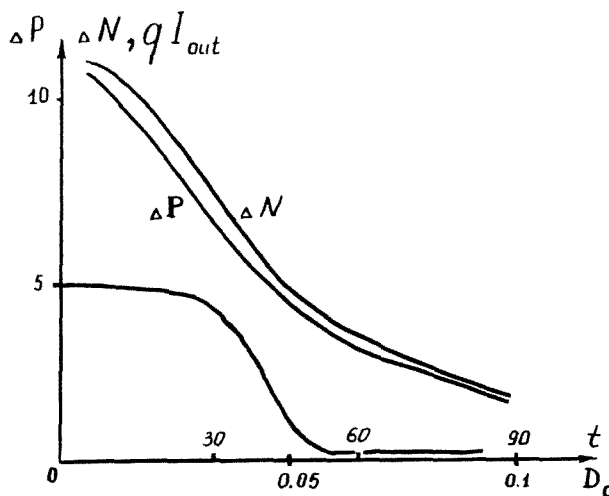

Fig. 7. Dependences of ΔP, ΔN from D_C and output radiation qP_{out} on the axis of the light beam in the case of explosive-like absorption.

$$\frac{\partial n}{\partial t} = \frac{R^2}{2} N_{B0} \exp(-1/T_m) - [(1 + N_{B0}) \exp(-1/T_m) + k \exp(-T_C/T_m)]n$$

$$+ \frac{N_0}{T_m^2} \exp(-1/T_m)(\Theta - \frac{R^2}{2} T_{out}),$$

$$\frac{\partial \Theta}{\partial t} = q\varphi(t)n\frac{2}{R^2} \int_0^R r\psi(r)\mathrm{d}r + \frac{6\eta_b}{(3 + \eta_b)R^2}\Theta + \frac{3\eta_b T_{out}}{3 + \eta_b} + \gamma\frac{\partial n}{\partial t}, \qquad (15)$$

with the initial conditions

$$n|_{t=0} = \frac{R^2}{2} N_{C0}, \qquad \Theta|_{t=0} = \frac{R^2}{2} T_{out}. \qquad (16)$$

Here $n = \int_0^R rN_C\,\mathrm{d}r$, $\Theta = \int_0^R rT\,\mathrm{d}r$ and $T_m = T_{out} + (0.4 - T_{out})/5$. Note that (15) and (16) are a result of the integration of (3) and (4) by the transverse coordinate.

The system (15), (16) can be solved analytically. We defined the length of the first phase (t_{ex}) as time, when $\Theta = 0.2R^2$. As it was shown in ref. [16] there exist the following dependences of t_{ex} on the main parameters:

$$t_{ex} \cong q^{-1} \ln(\mathrm{const}_q^{(1)}/(q + \mathrm{const}_q^{(2)})),$$

$$t_{ex} \cong \eta_b \ln(\mathrm{const}_{\eta_b}^{(1)} \eta_b^2/(\mathrm{const}_{\eta_b}^{(2)} + \eta_b)^2),$$

$$t_{ex} \cong \ln(\mathrm{const}_R^{(1)} R^2/(R^2 + \mathrm{const}_R^{(2)})).$$

Here $\mathrm{const}_u^{(1)}$, $\mathrm{const}_u^{(2)}$ are variables, not dependent on u.

4.2. THE $T_C < 1$ CASE

4.2.1. Numerical simulation [7,11]

The presence of the diffusion of gas components introduces some changes in the process of localization of the reaction (it is illustrated in fig. 8, which shows the dependences of the concentration of the reaction product for the following values of the parameters: $\eta_b = 10$, $T_C = 0.375$, $q = 10$, $\epsilon = 10$, $D_{A,B,C} = 0.01$). As in the case of spatially uniform beams, localization may occur if $T_C < 1$ and provided that there is preferential absorption of the optical radiation by the reaction product. However, on account of heat diffusion and the diffusion of gas components, the concentration localization over the transverse coordinate, which is formed initially, moves towards the lateral boundary. This is due to the fact that, at the beginning of the light pulse action on the gas, the temperature of the medium rises more quickly on the axis of the Gaussian beam. It leads to an acceleration of the chemical reaction and to further increase in the absorption of optical energy. Then the influence of heat diffusion and the diffusion of components increase and as a result the high temperature region expands and the localization boundary moves
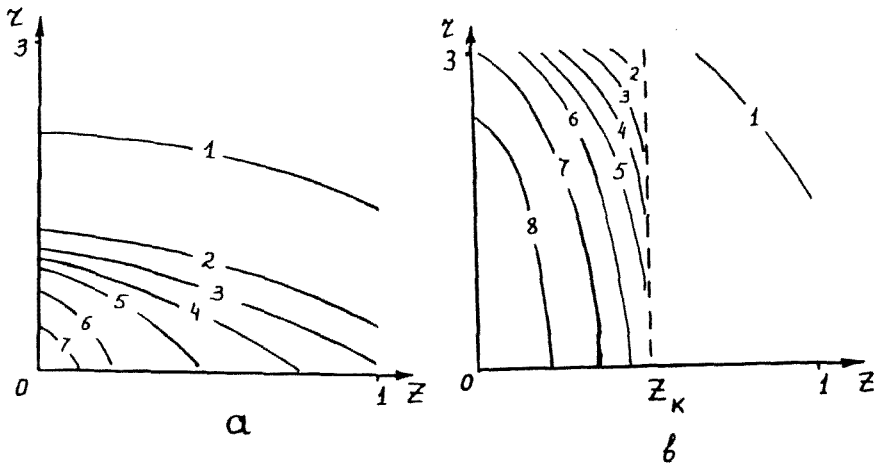
Fig. 8. Space distribution of N_C for $t = 30$ (a), 225 (b). Here $N_C = 0.01$ (1), 0.05 (2), 0.1 (3), 0.15 (4), 0.2 (5), 0.25 (6), 0.35 (7), 0.4 (8).

towards the boundary of the medium. This leads to its disappearance. We would like to emphasize that the concentration localizations on r and z are formed at different points in time, and can be observed simultaneously only for a particular choice of the beam radius, on which depends the heat diffusion time.

A two-component mixture of gases as also considered. The choice of analyzing the case of three components is due to the fact that here the observed processes are manifested for a wider set of parameters and initial conditions.

One further distinguishing feature of a three-component mixture compared with a two-component mixture is its greater sensitivity to differences in the values of the coefficients of diffusion $D_{A,B,C}$. Thus, whereas for a two- component mixture of gases a several-fold change in the product diffusion compared with D_A does not have any influence on the dynamics of the chemical reaction, for a mixture of three gases such a change leads to a substantial change in the processes, as illustrated in fig. 7, which shows the dependence of two localization parameters – the change in the reaction product in the centre of the region $\Delta N = N_C(0, z_k - 0, \tau = \infty)$ $/N_C(0, z_k + 0, \tau = \infty)$ and the N_C integral over r $\Delta P = \int_0^R N_C(0, z_k - 0, \tau = \infty) r \mathrm{d}r$ $/ \int_0^R N_C(0, z_k + 0, \tau = \infty) r \mathrm{d}r$ – on the ratio of the coefficients of diffusion for constant values of the remaining parameters.

As can be seen from the figure, on increasing the coefficient of the reaction product diffusion, the effect of its localization disappears. In addition to the decrease in ΔN and ΔP with an increase in D_C (for instance, $D_{A,B} = 0.02$) the maximum value of the concentration of the reaction product $N_C(z = 0, r = 0)$ decreases. Thus, for $D_C = 0.1$ the maximum value decreases by a factor of 3 compared with the value for $D_C = 0.02$. It is significant that the length of the efficient reaction zone

does not depend on the coefficient of diffusion of the reaction product. But the stationary value of qI on the beam axis at the bottom of the medium is roughly equal to 0.18 in the case of substances with equal coefficients of diffusion, and $qI = 0.35$ for $D_C = 0.1$. Thus, this results lead to the conclusion that an increase in the coefficient of diffusion of reaction products leads to a limitation on the concentration of the product because of a decrease in the time of interaction with the laser radiation. Consequently, the input intensity of the beam should increase with a rise in D_C.

The presence of bistability leads to one more interesting feature in the case of an optically thick cell: if the beam intensity at the input to the medium changes within wide limits, its output value remains practically constant (see fig. 9). This is due to the fact that the region of effective chemical reaction ($z < z_k$) becomes larger with an increase in the initial intensity, which leads to an increase in the absorption of optical radiation. If the initial intensity of the light beam is such that the length of the region of the effective reaction exceeds the length of the cell, then illumination of the medium commences. This effect may be used, for example, to produce pulses with a uniform time profile. In contrast to absorbers on dyes, in the present case only part of the radiation is absorbed, which for some problems is extremely advantageous.
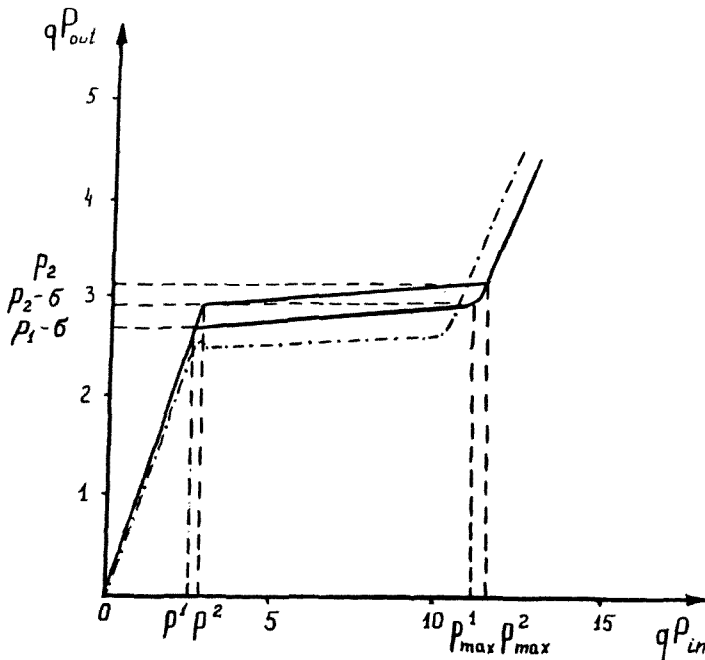

Fig. 9. Dependence of output radiation power on its input value. Numerical simulation (dash-dotted line); analytical study (solid line).

We shall describe now the influence of the thermal effect ($\gamma \neq 0$) of the reaction on the system dynamics. We recall that, according to the laws of thermal dynamics, for $T_C > 1$ the reaction proceeds with release of heat $\gamma > 0$, and for $T_C < 1$ the reaction proceeds with absorption of heat $\gamma < 0$. In the case when the coefficients of diffusion are equal ($D_{A,B,C} = 0.01$), $T_C = 0.375$ and the reaction product absorbs the laser radiation, its thermal effect ($\gamma = -3.3$) leads to some decrease in N_C on the beam axis at the point $z = 0$ and to a substantially sharper drop in the concentration of product along the z axis. At the same time, the region of the efficient reaction along the z axis does not decrease. However, in that case there is no plateau-shaped section of the dependence of N_C on z (for $r = 0$); the maximum value of the overall yield of the reaction P_C decreases, and N_C decreases practically according to a linear law with an increase in z to z_k. The maximum intensity at the output from the medium increases by a factor of 1.5.

4.2.2. Analytical study of output radiation stabilization [16]

As it has already been noted, bistable dependence of N_C on qI leads to stabilization of output radiation. In this section we shall describe one of the methods for the analytical study of this effect.

Thus, for steady distribution we can obtain the following dependence of radiation power $qP(P = \int_0^R rI(r, z, t = \infty)dr)$ on n:

$$qP = (1 - T_C)\ln^{-1}[(N_{B0} - 2n/R^2)(1 - 2n/R^2)/(2kn)] - T_{out})\eta_b$$
$$/(n\delta_C + (0.5R^2 N_{B0} - n)\delta_B + (0.5R^2 - n)\delta_A)). \qquad (17)$$

Equation (17) is written under the suggestion that $D_A \cong D_B \cong D_C$. In the case of stabilization this dependence is shown in fig. 2. As a result, near the boundary of the effective absorption region ($z = z_k$) light power $qP \in [p_1, p_2]$. At the same time, output radiation $qP_{out} = qP|_{z=1} \in [p_1 - \sigma, p_2 - \sigma]$. Here σ is an absorption out of the region of efficient chemical reaction, $\sigma \cong \exp(N_0(1 - z_k)\delta/2) \ll 1$, N_0 can be found from the condition of steady chemical reaction at $T = T_{out}$:

$$(1 - N_0)(N_{A0} - N_0)\exp(-1/T_{out}) - kN_0 \exp(-T_C/T_{out}) = 0. \qquad (18)$$

Now we will describe the stabilization of output radiation. Suppose that initially $q\phi(t) \int_0^R r\psi(r)dr = qP_{in} < p_2$ and the absorption is very small. After a slow increase in qP_{in} (the rate of increase is less than the rate of change in concentration and temperature) the chemical reaction becomes efficient in the region $qP > p_2$. Further increasing of qP_{in} leads to the moving of the boundary z_k (where $qP = p_2$) to the end of the medium. After $z_k \geqslant 1$ ($qP_{in} \geqslant p_{max}^2$) the absorption stabilizes (fig. 9) and the output radiation begins to increase again.

In the case of input radiation decreasing there are some changes. Thus, the conditions of stabilization are following: $p_1 < qP_{in} < P_{max}^1$ (here P_{max}^1 can be found from the equation $qP_{out} = p_1$), and $qP_{out} \in [p_1 - \sigma, p_1]$.

5. Optically thin nonlinear two-component medium with thermal diffusion (5), (6)

The role of thermal diffusion should be considered in a similar way. First of all, the chemical reaction is considered for the case where the components experience diffusion only.

5.1. THE EFFECT OF THE DIFFUSION COEFFICIENT RATIO OF GAS COMPONENTS ON THE REACTION EFFICIENCY

First of all consider the case where a beam of light propagates in a chemically active medium with $\alpha = \gamma = 0$. We shall consider a beam with $q = 15$ and gases with the diffusion coefficients $0.01 \leqslant D_{A,C} \leqslant 0.1$. The calculations show that with the increase of the diffusion coefficient ratio (denoted as $D = D_A/D_C$), the concentration N_C at the beam axis at $D = 10$ is by a factor of 1.5 higher than for $D = 1$. Far from the vessel centre the change in concentration with increase in D becomes fully marked. If $D < 1$, the concentration of the reaction product both at the vessel centre and close to its side surface rapidly decrease with D_C. These phenomena can readily be explained if it is recalled that the optical radiation is absorbed by the reaction product. Indeed, an increase in the ratio of the diffusion coefficients of the initial substance and the reaction product indicates an increase of the inflow of gas A from the region not occupied by the beam and at the same time a decrease of the rate of gas C outflow. This is equivalent to an increase in the rate of the forward reaction and in the temperature of the medium (fig. 10). In the mixture of such gases, the distributions of the reaction product and temperature acquire a character close to Gaussian whereas the distribution of the initial substance is close to homogeneous. Thus the beam of light that exist from such a medium acquires a circular profile since

$$I(z = \text{const}) = I(z = 0) \exp(-\text{const}\delta_C N_C).$$

Note also that the time necessary for attainment of the steady distribution of $N_{A,C}$ and T with an increase in D is long compared with that for the case $D = 1$ (fig. 10).

If $D < 1$, the concentration curves become different. Thus with a decrease of D down to 0.3, the distributions of concentration N_C and T are close to Gaussian, whereas the distribution of concentration N_A is close to $a(1 - \exp(-r^2)b)$, where a and b are certain constants. It is interesting that there exists a certain range of D values in which with a decrease in D, the concentration of the initial substance at the axis decreases whereas with the approach to the side surface of the vessel $(r = R)$ it increases and reaches a value exceeding unity. such a dependence of N_A is explained by different diffusion rates of the components. Note also that such an effect (i.e. the appearance of the region of lower N_A concentration in the heating zone and the higher concentration of this gas at the vessel walls) is also observed for
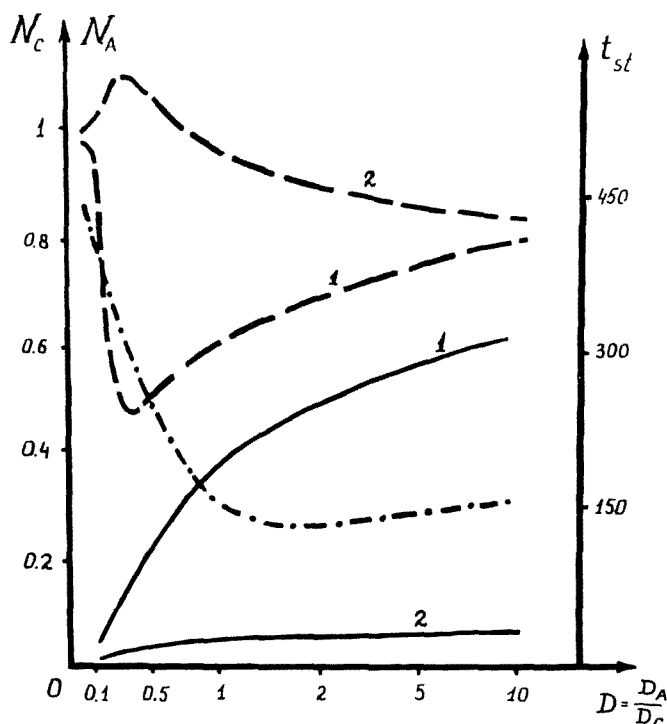
Fig. 10. Concentrations of the reaction product (solid lines) and initial substance (dashed line) and the time necessary for the attainment of the stationary state (dash- dotted line) versus the diffusion coefficient ratio. Curves 1 correspond to $r = 0$ and curves 2 correspond to $r = R$.

the mixture of light and heavy gases with allowance for their thermal diffusion: the heavy gas is likely to leave the heated region. With the further decrease of $D (D = 1/7, 0.1)$, the N_A and N_C profiles become close to homogeneous.

Concluding the consideration of this particular case, we should like to emphasize that the profile of the initial Gaussian beam will change at the exit from the medium and acquire a rectangular shape for $D = 0.3, 0.4$, whereas for $D < 0.2$ the profile will not change.

5.2. EFFECT OF THERMAL DIFFUSION ON THE REACTION KINETICS (THE $\alpha > 0$ CASE

5.2.1. Steady structures $(D_A < D_C, \alpha > 0)$

For instance, let our system be described by the following parameters: $\alpha = 0.2$, $D_A = 0.01$, $D_C = 0.1$, $q = 15$, $\epsilon = 10$, $\eta_e = 2$, $\gamma = 0$. Two circumstances are significant in that case: firstly, the influence of thermal diffusion for gas A is much stronger because of its weak diffusion; secondly, the thermal diffusion influence at different points of the vessel can be quite variable because of its dependence on N_A,

N_C and T. For $\alpha > 0$, thermal diffusion increases the outflow of the reaction product from the region of high temperature. In this case, the chemical reaction is not efficient enough, and N_C is very small ($\cong 10^2$). The occurrence of the chemical reaction can be increased in two ways. We can increase the radiation power q, or change the beam profile. Higher temperature leads to the active occurrence of the chemical reaction in both cases.

Consider the case $q = 60$ with a circular beam profile. The temperature of the gases is much higher in this case and the chemical reaction is vigorous, but the stationary distributions of $N_{A,C}$ are changed. Active diffusion of N_C with positive thermal diffusion leads to a homogeneous profile of the reaction product. As for the initial substance, its concentration changes along r (fig. 11). As a result of N_A inflow into the region of high temperature, the concentration of gas A begins to increase from $r = 2.5$ towards the beam axis and reaches its maximum at $r = 1.1$. After that, the concentration of gas A decreases because of a smaller temperature gradient and an efficient forward reaction. The maximum of N_A is situated near the beam boundary ($r = 1.5$), where the forward reaction is not efficient enough whereas the inflow of gas A caused by thermal diffusion is quite active.

Besides, the same results can be achieved for a Gaussian beam with $q = 50$, $\epsilon = 30$ and $\eta_e = 6$. Such values mean that the influence of heat diffusion is three times less than in the previous case. As a result, this distribution can be shown for Gaussian beams too (fig. 11). The maximum N_A value is more than 1 (curve 2); with a further decrease of the heat influence ($q = 150$, $\epsilon = 100$, $\eta_e = 20$) N_A achieves the value 1.1 (curve 3). Moreover, in that case N_A has another maximum near the vessel boundary. For $r > 2.5$, T is close to T_{out} and thermal diffusion is very small.
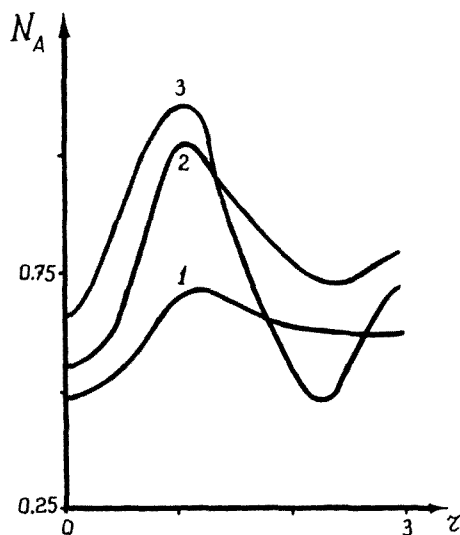

Fig. 11. Steady structures in the case of $D_A < D_C$, $\alpha > 0$.

That is why thermal diffusion increases the outflow of the initial substance from the region $2 < r < 2.5$ only. It lead to the decrease of N_A near $r = 2.25$. Note that in all cases the concentration N_C has a homogeneous distribution, but the maximum N_A coordinate is the same. If the radius of the vessel is much more than that of the beam, this effect can vanish because of a product reaction outflow from the small region of high temperature and efficient direct reaction out of this region.

Concluding this section we would like to remark that the heat effect of the chemical reaction leads to a decrease of temperature gradients and after $|\gamma| > \gamma_{cr}$ the distribution of N_A vanishes.

5.2.2. Separation of components ($D_C < D_A, \alpha > 0$)

This section includes results of a simulation of a gas mixture with converse diffusion coefficient ratio to that in the previous section. For instance, consider the following parameters: $q = 300$, $D_A = 0.1$, $D_C = 0.01$, $\epsilon = 50$, $\alpha = 0.2$, $\eta_e = 10$, $\gamma = 0$ and a circular beam profile.

To explain the changes observed in this case one should take into consideration that, qualitatively, the temperature profile always "repeats" the beam (fig. 12). Then, for $\alpha > 0$ the reaction product outflows from the heating region that coincides with the region of maximum radiation. Moreover, the initial gas distribution is close to homogenous because of its diffusion, whereas the influence of diffusion
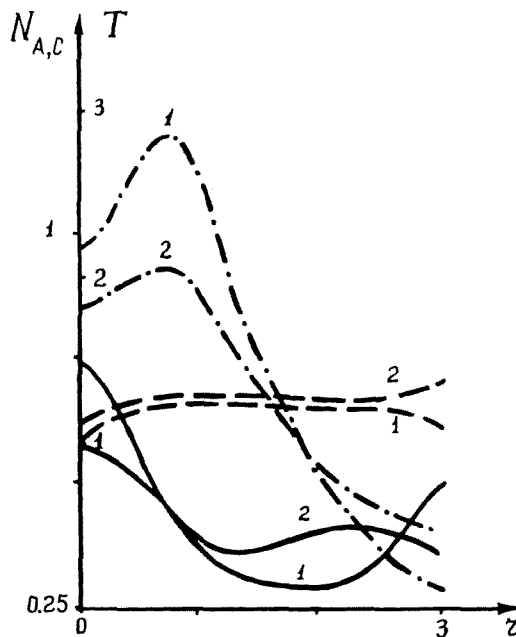

Fig. 12. Separation of components ($D_A > D_C, \alpha > 0$), N_C (solid line), N_A (dashed line), T (dash-dotted line). Curves 1 correspond to $\gamma = 0$ and curves 2 correspond to $\gamma = -35$.

upon the N_C distribution is insignificant. In this case, an important role in the formation of the concentration distribution is played by the distance from the region of high temperature to the surface of the cylinder or, for circular beams, also to the beam axis. Under certain conditions, the reaction product and the initial substance can be separated. The main feature of such a process is the accumulation of component C outside the region of its formation (fig. 12). Such a distribution is formed due to active product thermal diffusion from the high temperature zone of the occurrence of the forward reaction. As a result of the decrease of temperature towards the vessel boundary and beam axis the revers reaction is not efficient enough and so the concentration of N_C increases. Since the vessel is closed with respect to mass exchange even through its wall is not far from the region of efficient reaction, the concentration distribution takes the shape shown in fig. 4. If the vessel walls were permeable the process would have been accompanied by product separation from the vessel. This effect could also be used for the separation and purification of various gas mixtures.

In the case of the heat effect of the reaction ($\gamma < 0$) the temperature gradient decreases. The influence of thermal diffusion is then less than for $\gamma = 0$, and the distribution of N_C is more homogeneous (fig. 12). As for Gaussian beams we have only one region of N_C accumulation (near the vessel boundary), whereas well processes are the same.

5.3. EFFECT OF THERMAL DIFFUSION ON THE REACTION KINETICS (THE $\alpha < 0$ CASE)

In the previous section we have considered the situation in which the reaction product was a gas heavier than the initial substance. Now consider the reverse situation in which the molecular mass of the initial substance exceeds the mass of the reaction product. In the case of an inhomogeneous temperature profile the component C inflows into the high temperature region because of thermal diffusion. As a result, the radiation absorption at $\delta_C = 1$ and $\delta_A = 0$ becomes more pronounced and consequently T also increases. Since at $T_C < 1$ such a process shifts the equilibrium towards the forward reaction, one can draw the conclusion that thermal diffusion in this case promotes the forward relation between the temperature and the product concentration. As a result, the maximum N_C value increases whereas the region of the vigorous reaction becomes more localized with respect to r. Although the total amount of component C in the medium remains almost unchanged, its proportion in the beam center drastically increases. The existence of the local relationship between the components limits the maximum N_C value to N_{A0}, therefore a further increase of $|\alpha|$ produces no strong effect on the processes occurring in the medium. An interesting feature of the situation is that N_C reaches its maximum value not at the beam axis (which seems to be natural for the Gaussian case and is really observed for $\alpha = 0$) but in a certain beam cross section r_m. This can be explained, if it is taken into account that the maximum absolute value

of thermal diffusion is attained at the boundary between the high temperature region and the region of product formation. On approaching the beam axis, thermal diffusion becomes more feeble. As a result of N_C drawing into the region of product localization the reverse reaction proceeds more vigorously and the concentration N_C decreases with the weakening of thermal diffusion.

In the absence of the local relationship between the components (e.g. $D_C = 0.01$, $D_A = 0.1$, $\alpha = -0.2$) the changes in the system behavior are of a more pronounced character. In this case the enhancement of diffusion results in a more homogeneous distribution of component A over the volume, which enhances thermal diffusion. A more active inflow of the initial substance to the central region additionally activates the forward reaction close to the beam axis. This increases absorption and the temperature gradient, which in turn, further enhances thermal diffusion. As a result, the process acquires an avalanche-type character, where thermal diffusion plays the main role. An increase in N_C results in activation of the reverse reaction and N_C continues to increase at the expense of thermal diffusion. In turn, the initial substance, formed due to a higher rate of the reverse reaction, is efficiently removed from this region. It should be emphasized that in this case an important role is played by the characteristic times of diffusion, thermodiffusion, chemical reaction and medium heating processes. It is the relationship between these processes that controls the overall process. As a result, in the center of such a region N_C forms a "peak" whose appearance precedes a change in temperature.

The further increase of N_C at the beam axis strongly increases the radiation absorption and temperature. But the diffusion process results in a gradual enlargement of the high temperature region and a decrease of the T gradient. This, in turn, reduces thermodiffusion and the maximum N_C value at the beam axis because of the vigorous reverse reaction and growth in N_C outside the initial maximum region. The radiation absorption at the beam axis becomes less pronounced, there is a further reduction of the T gradient and the thermal diffusion flux is observed. As a result of such processes the system acquires a steady state with substantially more homogeneous concentration and temperature distribution (fig. 13).

The most interesting feature of the case $\alpha < 0$, $D_C < D_A$, is a new role of the thermal effect of the reaction. As has been shown in ref. [3] and in some other studies, the thermal effect "smooths" the inhomogeneities of N_A, N_C and T distributions and promotes the stability of the stationary states of the system. But in the case under consideration the thermal effect plays quite a different role. As has already been noted, in the zone of high product concentration the reverse reaction proceeds vigorously ($f < 0$) whereas at the boundary of the zone an active formation of the product occurs which is then drawn into the peak zone due to thermal diffusion. If $\gamma < 0$ (and it is just the case for $T_C < 1$), this results in an additional heat release at the beam axis and in a strong cooling at the boundary of the efficient reaction zone. Such a process prevents the broadening of the high-temperature zone due to diffusion. It has already been noted that the transition at $\alpha \leqslant 0$ to smoother distributions occurs due to weakened thermal diffusion caused by the change of the
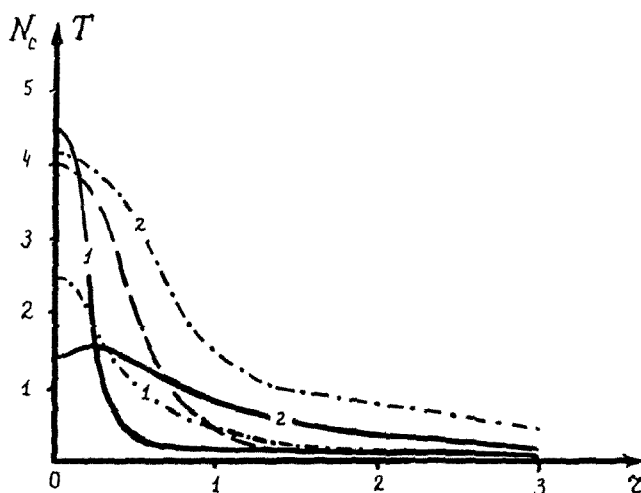
Fig. 13. N_C (solid line) and temperature (dash-dotted line) profiles at the moment of attaining the maximum value of the product concentration ($t = 52$) (curves 1), for steady distribution (curves 2) at $\gamma = 0$, and the product profile for the steady mode at $\gamma = -7$ (dashed line). The other parameters have the values: $T_C = 0.375, D_A = 0.01, k = 1, \epsilon = 10, q = 15, \delta_A = 0, \delta_C = 1, \eta_e = 2$.

temperature profile. In the case of $\gamma < 0$ such a process cannot occur because of the above considered reasons. Thus, the peak of the product concentration is stabilized and no smoothing of the distributions occurs. This is illustrated in fig. 13, which shows the steady N_C distribution for $\gamma = -7$. It is seen that the thermal effect substantially enhances the distribution inhomogeneities.

It should also be noted that analogous processes also take place for mixtures characterized by the local component relationships. But if the diffusion coefficients are different, these processes are better pronounced. It should also be emphasized that the initial Gaussian beam acquires a circular profile when leaving the medium with a clearly visible decrease in intensity at the beam axis. Since the peak diameter is relatively small, various diffraction phenomena can be observed which deserve a special consideration.

If $\alpha < 0$ and $D_C > D_A$ no peak is observed. Instead there are periodic oscillations with a decreasing amplitude. As is seen from the restrictions imposed on the system parameters, the only distinction from the case of N_C distribution with a peak is the inverse ratio of diffusion coefficients. In the region of efficient reaction, the more intense C diffusion results in a constant deficiency of the initial substance, which results in the appearance of oscillation cycles described below. First, the occurrence of the forward reaction and the drawing-in effect of thermal diffusion result in an increase of N_C at the beam axis, the process being accompanied by stronger radiation absorption and temperature rise. At the same time, thermal diffusion provides the removal of the initial substance. Since the diffusion of compo-

nent A is relatively weak, a region is formed at the beam axis where the amount of component A is very small, which activates the reverse reaction. This process is accompanied by a decrease in N_C, which, in turn, decreases the temperature and increases the concentration of the initial substance due to weakened thermal diffusion. Then the whole cycle proceeds anew. As a result, the damping oscillations with a decreasing amplitude are formed in the medium.

It should be emphasized that in the case of $\alpha < 0$ an important role is played by the relationship of the characteristic times of the processes occurring in the medium. The space of the characteristic times can be divided into regions where different modes of the system behavior are realized. In our opinion, this problem is very interesting and requires a more detailed consideration in the future.

6. Numerical methods [15,16,18]

Consider briefly the problems encountered in the numerical solution of systems (1)–(6). In what follows we shall apply the notation used in the theory of finite difference schemes.

While calculating chemical reactions in a medium, we used the implicit difference schemes on a time and space uniform grid that provided a second order approximation in space and a first order one in time. In order to find a solution in a new temporal layer, we used the simple iteration method combined with the run along the space coordinates. The following theorems were proved:

THEOREM 1 [SYSTEM (1), (2)]

1. A simple iteration method converges in the grid's norm C like a geometric progression with a speed $(C_1\tau)^m$, if $\tau < C_1$. Here m is the number of iterations and τ the time step.
2. The solution of the finite difference scheme converges to a solution of the system (1), (2) in the grid's norm C with a speed $O(\tau + h_z^2)$.
   Here $\|U\|_C = \max_i |U(r_i, t)|$, i is a point along the coordinate z and h_z is the step along z.

THEOREM 2 [SYSTEM (3), (4)]

1. A simple iteration method converges in the grid's norm C like a geometric progression with a speed $(C_1\tau)^m$, if $\tau < C_1$.
2. The solution of the finite difference scheme converges to a solution of the system (3), (4) in grid's norm L_2 with a speed $O(\tau + h_r^2(\ln(h_r^{-1}))^{0.5} + h_z^2)$.
   Here $\|U\|_{L_2}^2 = \sum_{i=1}^{N_r-1} U^2(r_i, t) r_i h_r$, i is the number of a point along the transverse coordinate, h_z is the step along z and h_r is the step along r.

THEOREM 3 [SYSTEM (5), (6)]

1. A simple iteration method converges in the grid's norm L_2 like a geometric progression with a speed $(C_1\tau/h_r)^m$, if $\tau < h_r/C_1$. Here m is the number of iterations, τ is the time step, and h_r is the step in space.

2. The solution of the finite difference scheme converges to a solution of the system (5), (6) in the grid's norm L_2 with a speed $O(\tau + h_r^2(\ln(h_r^{-1}))^{0.5})$ if $\tau < h_r/C_2$.

Here $\|U\|_{L_2}^2 = \sum_{i=1}^{N_r-1} U^2(r_i, t)r_i h_r$, i is the number of a point along the transverse coordinate.

The calculation for the case $\alpha < 0$ is complicated because of possible realization of modes with fast changes in N_C in a region with small r (section 5). Therefore the step should be reduced because of the necessity, firstly, of following a local structure occupying 5–15% of the whole volume, and, secondly, of fulfilling conditions of function nonnegativity and stability of the P invariant. Thus for modes with relatively smooth spatial distributions these conditions are fulfilled for sufficiently small number of points ($h_r \cong 0.1$). But in some cases (see section 5) the steps should be of the order of 10^{-2}. But the use of homogeneous grids in this case seems to be useless because of a large number of points in the region of the smooth solution, which results in substantial increase of the required computational time. The situation may be improved by the use of the grids with a variable step widely used in practice in combination with their rearrangement with time, i.e. the use of solution-adaptive grids. The use of such grids thus allows a reduction in our calculations of the point number by 3–5 times as compared to homogeneous grids. But in this case one should interpolate the obtained solutions from one grid to another.

One of the possible methods of the adaptive grid construction is described in ref. [18]. The calculations show that in order to achieve the required accuracy in the solution of the given problem, it is expedient to use the following criterion:

$$h_r^{-2} \cong r\frac{\partial^2}{\partial r^2}\left(D_C\frac{\partial N_C}{\partial r} + \alpha\frac{N_C N_A}{T}\frac{\partial T}{\partial r}\right).$$

We would like to emphasize that our aim in this section has been mainly to state the basic problems encountered in the simulation of processes under consideration and to indicate the method of their solution.

7. Conclusion

Thus, three models of laser radiation interaction with chemically active gas have been described in the present paper. Different types of nonlinear effects are investigated with the help of numerical simulation. Some aspects of practical application of these results have been discussed.

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