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PROPAGATION OF WEAK SHOCK WAVES IN MEDIA WITH AN ARBITRARY NUMBER OF CHEMICAL REACTIONS

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The problem of shock wave propagation from a piston advancing at constant velocity into a stationary equiponderant gas in which an arbitrary number of chemical reactions may take place, is considered. It is assumed that equilibrium and the frozen speeds of sound in the gas mixture are close to each other. It is shown that in gases with strongly differing reaction rates the shock wave region may be conditionally divided into zones in which reactions proceed independently. The singular nature of intermediate speeds of sound is revealed.

1. Input equations. As shown in [1, 2], the transmission of signals in relaxating mixtures is accompanied by dispersion, and in limit cases the transmission rate of these is the same as the equilibrium a_{e0} or the frozen a_{f0} speeds of sound. It is clear that in the case of media considered here the propagation velocity of acoustic waves does not greatly differ from these two speeds of sound.

In the piston problem it is possible to consider the motion of gas as a short wave and define it by the equation [3]

$$2(\varepsilon m_0 v - \varepsilon^2{}_\alpha \gamma_f)\frac{\partial v}{\partial r} - 2\Delta\frac{\partial v}{\partial t} = \varepsilon_\alpha{}^2 l\mathbf{e}\,\frac{\partial \mathbf{q}}{\partial r} \tag{1.1}$$

$$\partial q_i/\partial r = -L(\lambda_i q_i - e_i v), \quad i = 1, \ldots, N$$

Sometimes the analysis is more conveniently carried out using the equation obtained from (1.1) by eliminating parameters q_i [4]

$$\sum_{\mu=0}^{N}\sigma_\mu(L\lambda)\frac{\partial^{N-\mu}}{\partial r^{N-\mu}}\left[2(\varepsilon m_0 v - \varepsilon_\alpha{}^2\gamma_{N-\mu})\frac{\partial v}{\partial r} - 2\Delta\frac{\partial v}{\partial t}\right] = 0 \tag{1.2}$$

Let us reiterate the meaning of notation used in (1.1) and (1.2). By denoting the dimensional time and space variables by T and R, respectively, we obtain the equalities

$$r = (a_0 T - R)/L, \quad t = a_0 T\Delta / L$$

where a_0 is the moving coordinate system velocity related to the frozen and equilibrium speeds of sound by formulas

$$a_0 = a_0\varepsilon_a{}^2\gamma_{f0} + a_{f0} = a_0\varepsilon_a{}^2\gamma_{e0} + a_{e0}$$

The small parameter $\varepsilon_a{}^2$ defines the closeness to the speed of sound, and ε determines the amplitude of perturbations induced in the quiescent gas by the piston.

The perturbed dimensional velocity of gas is $\varepsilon a_0 v$, Δ is a small parameter associated with the assumption that the flow represents a short wave, and L is a characteristic length in the direction of the r-axis in the introduced moving system of coordinates.

The constants $l > 0, \lambda_i > 0, m_0 > 0$, and e_i depend on the physico-chemical properties of the considered gas. The variable q_i is proportional to the completeness of the i-th chemical reaction. Vector $\mathbf{q}=(q_1, \ldots, q_N)$ defines the composition of the gas mixture. In the Gibbs formula each quantity q_i as linked to the i-th reaction affinity ω_i which in the approximation considered here is of the form

$$\omega_i = \lambda_i q_i - e_i v \tag{1.3}$$

When the i-th reaction proceeds in equilibrium $\omega_i = 0$. The symbol $\sigma_l(x)$ denotes the sum of all possible products composed of numbers $x_1, \ldots, x_N$ taken in sets of l in each product. The quantities

$$\gamma_k = \gamma_{f0} - \frac{l}{2} \sum_{m=k+1}^{N} (-1)^{m-k} \frac{\sigma_{N-m}(\lambda)}{\sigma_{N-k}(\lambda)} \mathbf{e}\mathbf{D}^{m-k-1}\mathbf{e}$$

are of order unity and determine the intermediate speeds of sound in the gas by formulas $\alpha_k = a_0(1 - \varepsilon_a^2 \gamma_k)$, $\mathbf{D}$ is a diagonal matrix with elements $d_{ii} = \lambda_i$. For α_k we have the sequence of inequalities

$$a_{f0} = \alpha_N > \ldots > \alpha_0 = a_{e0}$$

The system of Eqs. (1.1) implies that each quantity $1 / \lambda_k$ may be taken as the characteristic length of the k-th chemical reaction. In this paper particular attention is given to gas mixtures in which chemical reaction rates differ considerably. This stipulation is satisfied when conditions

$$\lambda_1 \gg \lambda_2 \ldots \gg \lambda_N, \quad e_i^2 / \lambda_i \sim 1 \quad (i = 1, \ldots, N) \tag{1.4}$$

are satisfied.

In that case the following approximate equalities are valid:

$$\alpha_k = a_{f0}\left[1 - \frac{l}{2}\varepsilon_a^2 \sum_{i=1}^{N-k} \frac{e_i^2}{\lambda_i}\right] \tag{1.5}$$

It was shown in [5] that the quantities in the right-hand sides of the last equality are equal to k-multiply frozen and $(N-k)$-multiply equilibrium speeds of sound $a_{fe}^{(M)}$ which are calculated by formulas

$$(a_{fe}^{(M)})^2 = (\partial p / \partial \rho_0)_{q_1, \ldots, q_k, \omega_{k+1}, \ldots, \omega_N, s}$$

where s is the specific entropy of the gas mixture, and ρ and p are, respectively, its density and pressure. The subscript zero at a partial derivative indicates that it is calculated for a quiescent gas in equilibrium.

2. The steady traveling wave. Below we shall need some information about steady solutions of the system of Eqs. (1.1).

For this we set in (1.1) and (1.2) $\partial v / \partial t = 0$ and establish the following boundary conditions:

$$v = v_0, \; dv / dr = 0, \; dq_i / dr = 0, \quad r = +\infty \tag{2.1}$$

$$v = 0, \; dv / dr = 0, \; q_i = 0 \; dq_i / dr = 0, \quad r = -\infty$$

Integrating the first equation of system (1.1) and allowing for the conditions at infinity, in the steady case we obtain

$$\varepsilon m_0 \left(v - \frac{\varepsilon_a{}^2 \gamma_{f0}}{\varepsilon m_0}\right)^2 - \varepsilon_a{}^2 l \sum_{i=1}^{N} e_i q_i = \frac{\varepsilon_a{}^4 \gamma_{f0}{}^2}{\varepsilon m_0}$$

which at $+\infty$ yields the formula

$$v_0 = \frac{2\varepsilon_a{}^2 \gamma_{e0}}{\varepsilon m_0} \tag{2.2}$$

which links the propagation velocity of the steady traveling wave to the stream velocity at $+\infty$. To determine the asymptotic behavior of solution at $-\infty$ we set in system (1.1) in conformity with (2.1) $\partial v / \partial t = 0$ and make the quantities v and q_i and their derivatives tend to zero. Analysis of the derived system of linear equations shows that continuous solutions of this problem exist, if the following inequalities are satisfied:

$$\gamma_{e0} > 0 > \gamma_{f0} \tag{2.3}$$

When $\gamma_{f0} > 0$ a compression shock is formed in the flow field ahead of which the gas is free of perturbations. A limit solution with a point-characteristic at which the perturbed flow is separated from the quiescent background corresponds to condition $\gamma_{f0} = 0$. The inequality $\gamma_{e0} > 0$, as implied by (2.2), means that the steady traveling wave can only be a compression wave.

Let us derive the conditions at the shock front for discontinuous solution. We assume that the front is at point $r = 0$. Then, integrating the equations of system (1.1) from $-\delta$ to δ with $\partial v / \partial t = 0$ and δ a positive number which is made to tend to zero, for the flow parameters at the shock we obtain

$$v = \frac{2\varepsilon_a{}^2 \gamma_{f0}}{\varepsilon m_0}, \quad q_i = 0, \quad i = 1, \ldots, N$$

3. The problem of piston for two reactions. A shock wave induced by the moving piston propagates in the gas. Certain relationships must be satisfied at the wave front. We obtain these using system (1.1). The main parts of its equations are of divergent form, hence at the front defined implicitly by the equation $\varphi(r, t) = 0$ the following equalities are satisfied:

$$\left[\frac{(\varepsilon m_0 v - \varepsilon_a{}^2 \gamma_{f0})^2}{\varepsilon m_0}\right] \varphi_r - \Delta [v] \varphi_t = \frac{l \varepsilon_a{}^2}{2} \sum_{k=1}^{N} e_k [q_k] \varphi_r$$

$$[q_k] \varphi_k = 0, \quad k = 1, \ldots, N, \quad [f] = f_1 - f_2$$

where f_1 and f_2 are values of function f behind and ahead of the shock, respectively. Since the flow ahead of the shock wave is free of perturbations, we have

$$\varepsilon_a^2\gamma_{f0} - \frac{\varepsilon m_0 v_f}{2} = -\Delta\frac{\varphi_t}{\varphi_r} \tag{3.1}$$

$$q_{kf} = 0, \quad k = 1, \ldots, N$$

(Subscript f denotes parameters of flow at the shock front). By known rules of implicit function differentiation we have

$$-\frac{\varphi_t}{\varphi_r}\bigg|_{\varphi(r,t)=0} = \frac{dr_f}{dt}$$

which determines the propagation velocity of the shock front in dimensionless coordinates. Conditions (3.1) must be supplemented by the equality

$$v_p = 1 \tag{3.2}$$

which defines the dimensionless velocity of gas at the piston.

Results of numerical calculations of the problem (1.1), (3.1), (3.2) are shown by solid lines in Figs. 1 and 2 at various instants of time and $\varepsilon m_0 = 0.6$ (a), $\varepsilon m_0 = 0.3$ (b), and $\varepsilon m_0 = 0.1$ (c); ξ_i and ξ_0 are dimensionless space variables represented in the system of coordinates attached to the wave in scales $L = 1/\lambda_1$ and $L = 1/\lambda_2$, respectively. It was assumed that $N = 2$, $\lambda_1 = 100$, $\Delta = 0.1$, $e_1 = 10$, $\lambda_2 = 1$, $e_2 = 1$, $l = 2$, and $\varepsilon_a^2 = 0.1$. Curves *1*–*8* correspond to $t_i =$ 10, 20, 40, 80, 100, 140, 300, and 600.

On the basis of these calculations it is possible to state that in gas mixtures that satisfy conditions (1.4) the formation of the wave takes place as follows. It is possible to exclude initially from the analysis the second reaction and consider it as completely frozen. For fairly long times the solution represents a steady traveling wave for which it is necessary to set $v_0 = 1$ in conditions (2.1). As the time further increases the slow reaction begins to affect the flow field. The shock wave region can now be separated into two zones, in one of which the second reaction is completely frozen and the flow is determined by the fast reaction, while in the other only the second reaction takes place in an unsteady manner.

Let us consider these results from the point of view of the method of joining asymptotic expansions [6].

Since the initial gas flow is determined by the fast reaction, we set in Eq. (1.2) $L = 1/\lambda_1$. Disregarding in it the lower terms and integrating once, for the determination of velocity in the shock wave we obtain the equation

$$\frac{\partial}{\partial r}\left[(\varepsilon m_0 v - \varepsilon_a^2\gamma_{f0})\frac{\partial v}{\partial r} - \Delta\frac{\partial v}{\partial t}\right] + (\varepsilon m_0 v - \varepsilon_a^2\gamma_1)\frac{\partial v}{\partial r} - \Delta\frac{\partial v}{\partial t} = 0$$

Taking into account the limit formula (1.5) for the speeds of sound, we can ascertain that the obtained equation is equivalent to the system of equations

$$(\varepsilon m_0 v - \varepsilon_a^2\gamma_{f0})\frac{\partial v}{\partial r} - \Delta\frac{\partial v}{\partial t} = \frac{l\varepsilon_a^2}{2} e_1 \frac{\partial q_1}{\partial r} \tag{3.3}$$

$$\partial q_1/\partial r = -(\lambda_1 q_1 - e_1 v)/\lambda_1$$

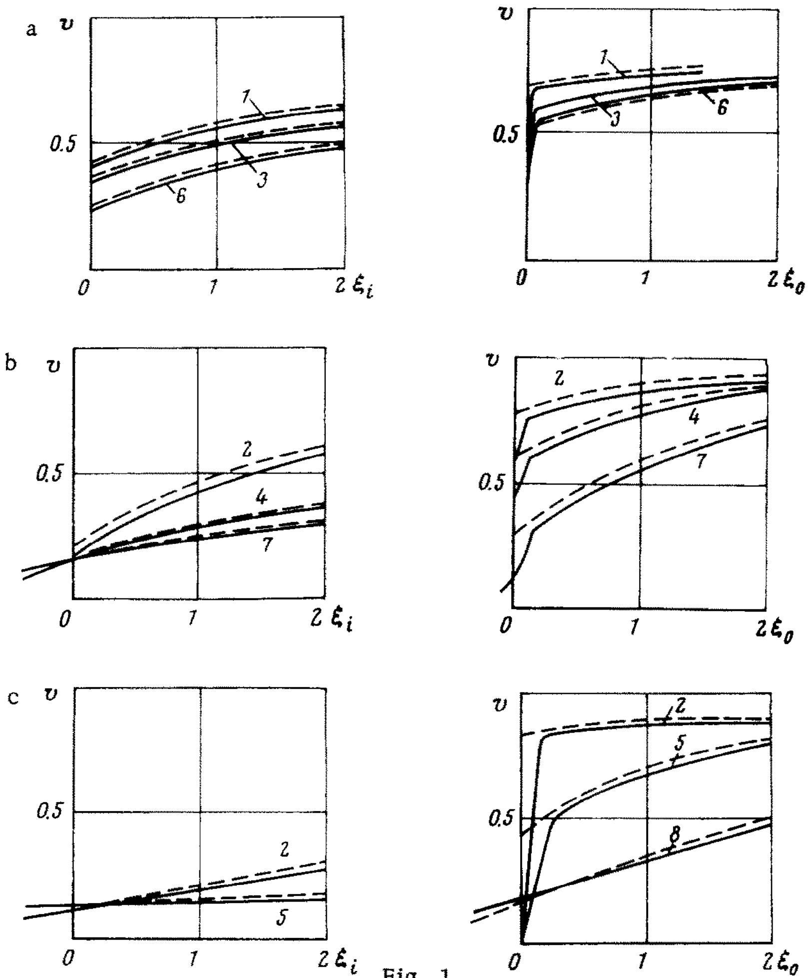

Fig. 1

This system together with boundary conditions (3.1) and (3.2) yields the solution of the problem of piston in a relaxing mixture in which only the first reaction proceeds, while the second is completely frozen. The first two of conditions (3.1) can be directly obtained from (3.3). For reasonably long times the solution of that problem yields a steady wave [7, 8], which in accordance with inequality (2.3) and depending on the relation between ε and ε_a^2 that wave is either partly or completely dispersed.

With further increase of time the slow reaction begins to affect the flow field. We call the region in which the transition of the first reaction to the equilibrium state takes place the relaxation zone of that reaction. The width of that zone in dimensionless coordinates related to the new scale $1 / \lambda_2$ [7] is

$$l_2 = \left(1 + \frac{1}{v_H} \frac{le_1^2}{2\lambda_1} \frac{\varepsilon_a^2}{\varepsilon m_0}\right) \frac{\lambda_2}{\lambda_1}$$

where v_H is related to the wave propagation velocity by equality (2.2).

If $l_2 \ll 1$, it is possible to introduce in the system of Eqs. (1.1) in new dimensionless variables an intermediate shock wave passing through which the first reaction reaches the equilibrium state defined by the condition $\omega_1 = 0$, and the composition of the second reaction remains unchanged.

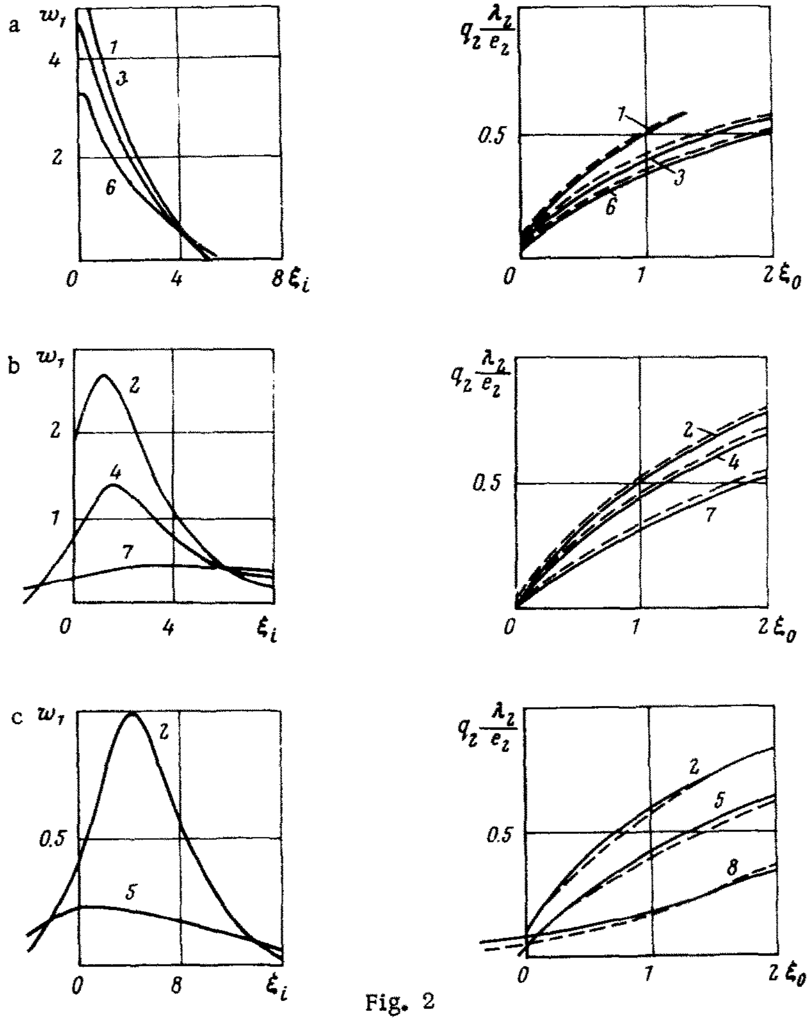

Fig. 2

From the condition of the first reaction equilibrium and (1.3) we obtain $\partial q_1 / \partial r = (e_1 / \lambda_1)\, \partial v / \partial r$. Substituting the obtained expression for $\partial q_1 / \partial r$ into the first equation of system (1.1) and taking into account the limit formulas for intermediate speeds of sound (1.5), we obtain the equations

$$(\varepsilon m_0 v - \varepsilon_a{}^2 \gamma_1) \frac{\partial v}{\partial r} - \Delta \frac{\partial v}{\partial t} = \frac{l \varepsilon_a{}^2}{2} e_2 \frac{\partial q_2}{\partial r} \qquad (3.4)$$

$$\frac{\partial q_2}{\partial r} = - \frac{\lambda_2 q_2 - e_2 v}{\lambda_2}$$

From this, similarly to (3.1), on the introduced intermediate shock wave we have the conditions

$$\varepsilon_a^2\gamma_1 - \frac{\varepsilon m_0 v_H}{2} = \Delta\frac{dr_H}{dt} = V_H, \quad q_{2H} = 0 \tag{3.5}$$

where the subscript H denotes variables at the intermediate shock wave. Note that the second of conditions (3.5) — obvious from the definition of the intermediate shock wave — is only a formal corollary of system (3.4).

Equations (3.4) together with conditions (3.5) and (3.2) are entirely analogous to the problem of piston in a mixture with a single reaction considered above. The intermediate speed of sound α_1 plays here the part of the frozen speed of sound, which is quite natural, considering that in this approximation $\alpha_1 = (\partial p / \partial \rho_0)_{\omega_1, q_2, s}$.

As is usual in the method of joining asymptotic expansions, we shall call the solution of problem (3.4), (3.5), (3.2) external, and the solution in the relaxation zone of the first reaction, the internal solution, which with their related dimensionless independent variables will be denoted by subscript 0 and i, respectively. The preceding analysis shows that the external solution can be obtained independently of the internal which is determined by the condition of its joining with the external solution.

We introduce the new dimensionless variable

$$\xi = r - \frac{1}{\Delta}\int_a^t V_H(\tau)\,d\tau$$

which is linked with the intermediate shock wave.

In the new variables (1.2) is of the form

$$\begin{aligned}&\frac{\partial^2}{\partial\xi^2}\left[(\varepsilon m_0 v - \varepsilon_a^2\gamma_{f0})\frac{\partial v}{\partial\xi} - \Delta\frac{\partial v}{\partial t} + V_H(t_0)\frac{\partial v}{\partial\xi}\right] + \\ &(L\lambda_1 + L\lambda_2)\frac{\partial}{\partial\xi}\left[(\varepsilon m_0 v - \varepsilon_a^2\gamma_1)\frac{\partial v}{\partial\xi} - \Delta\frac{\partial v}{\partial t} + V_H(t_0)\frac{\partial v}{\partial\xi}\right] + \\ &L^2\lambda_1\lambda_2\left[(\varepsilon m_0 v - \varepsilon_a^2\gamma_{e0})\frac{\partial v}{\partial\xi} - \Delta\frac{\partial v}{\partial t} + V_H(t_0)\frac{\partial v}{\partial\xi}\right] = 0\end{aligned} \tag{3.6}$$

The condition of joining external and internal solutions is

$$v_i(\xi_i, t_i) = v_H(t) \text{ when } \xi_i \to \infty \tag{3.7}$$

Since $v_H = v_H(t_0)$, the solution in the inner region is of the form

$$v_i = v_i(\xi_i, t_0)$$

Then setting in (3.6) $L = 1/\lambda_1$ and rejecting terms of higher order of smallness, for the determination of v_i we obtain the equation

$$\begin{aligned}&\frac{\partial}{\partial\xi_i}\left[\left(m_0\varepsilon v_i - \varepsilon_a^2\gamma_{f0} + \varepsilon_a^2\gamma_1 - \frac{\varepsilon m_0 v_H}{2}\right)\frac{\partial v_i}{\partial\xi_i}\right] + \\ &\left(m_0\varepsilon v_i - \frac{\varepsilon m_0 v_i}{2}\right)\frac{\partial v_i}{\partial\xi_i} = 0\end{aligned}$$

which is entirely analogous to the equation that defines the structure of a steady shock wave in a gas with a single chemical reaction but contains the term $v_H(t_0)$ which depends on time t_0. It is seen from (2.2) that the solution of that equation actually satisfies the condition of joining (3.7). In conformity with inequality (2.3), when $\frac{1}{2}\varepsilon m_0 v_H + \varepsilon_a^2 \times (\gamma_{f0} - \gamma_1) < 0$ (> 0) the internal solution is a wave with complete (partial) dispersion.

We thus conclude that the flow field separates into two fields. In the external field the first reaction is in complete equilibrium and the solution there is determined by the slow reaction. In the internal region the flow is quasi-steady: its solution at any instant of time is of the same form as the steady solution, but its parameters depend on time t_0. There the second reaction is frozen.

If at the limit $t_0 \to \infty$ the external solution represents a steady traveling wave with partial dispersion and v_H at its front satisfies the condition $l_2 \ll 1$, the above analysis is valid for all t_0, and the complete solution is a steady traveling wave when $t_0 \to \infty$. It is seen that the region of stable flow can also be divided in two zones in which the reactions proceed independently in the meaning described above.

When v_H at the intermediate shock wave becomes so small that the condition $l_2 \ll 1$ is no longer valid, that analysis is inapplicable, since then a region in which the interaction of reactions is substantial appears in the flow field.

Let us derive the equation which determines the gas velocity in that region. It follows from (3.5) that in the initial dimensional coordinates that velocity is close to α_1. Hence we set in (1.2) $\gamma_1 = 0$. Since v is small, we neglect in (1.2) lower terms and obtain

$$-\varepsilon_a^2 \gamma_{f0} \frac{\partial^2 v}{\partial r^2} + L\lambda_1 \left(\varepsilon m_0 v \frac{\partial v}{\partial r} - \Delta \frac{\partial v}{\partial t}\right) - L^2 \lambda_1 \lambda_2 \varepsilon_a^2 \gamma_{e0} v = 0$$

The pattern of behavior of the mixture parameters in the interaction region can only be analyzed by solving the complete problem of piston. However the last equation makes it possible to obtain a qualitative idea about the formation of the steady traveling wave when for considerable t_0 the condition $l_2 \ll 1$ is no longer valid. If the propagation velocity in the steady solution for the external region is close to α_1, the effect of the interaction region propagating at velocity α_1 is substantial and, at least, the "tail" of the stabilized steady traveling wave in the complete problem of piston is determined by both reactions. But when the propagation velocity in the steady solution for the external region is not close to the speed of sound α_1 and is below it, the wave packets of the external region and that of reaction interplay disperse in space. The solution in the reaction interaction region attenuates with time in conformity with an exponential law, while in the external region it becomes a steady solution. In a stabilized steady traveling wave the first reaction is in complete equilibrium. It follows from Sect. 2 that in the stable equation that defines such wave $\gamma_1 < 0$.

For the sake of comparison asymptotic solutions shown by dash lines are plotted in Figs. 1 and 2 besides the numerical solution of the complete problem (1.1), (3.1), (3.2).

4. Shock wave structure in the case of an arbitrary number of chemical reactions. The analysis presented here can, by analogy, be applied to gas mixtures with an arbitrary number N of chemical reaction taking place in it. We shall extend to such case the conclusions reached about steady solution of the problem (1.1), (2.1).

If $\gamma_{f0} \geqslant 0$, the flow can be separated into N zones. Solution in the

k- th is determined by the k- th reaction. The first ($k-1$)-st reactions in that zone are in equilibrium, and reactions numbered $k+1, \ldots, N$ are frozen. The quantities v and q_k are determined here by the equations

$$2(\varepsilon m_0 v - \varepsilon_a^2 \gamma_{N-k+1}) \frac{dv}{dr} = l\varepsilon_a^2 \frac{dq_k}{dr} \tag{4.1}$$

$$\frac{dq_k}{dr} = -\frac{\lambda_k q_k - e_k v}{\lambda_k}$$

Integration of this system is carried out for initial conditions

$$v\,|_{r=0} = \frac{2\varepsilon_a^2\gamma_{N-k+1}}{\varepsilon m_0}, \quad q_k\,|_{r=0} = 0 \tag{4.2}$$

Recalling the limit formulas for intermediate speeds of sound, from this and equality (2.2) we obtain

$$v = \frac{2\varepsilon_a^2\gamma_{N-k}}{\varepsilon m_0}, \quad r = \infty \tag{4.3}$$

It follows from (4.2) and (4.3) that the principle of joining is satisfied in the derived solution.

Let in Eq. (2.1) $\gamma_{f0} < 0$, then owing to the monotonicity of intermediate speeds of sound noted in Sect. 1, there exists such $k \geqslant 1$ that

$$\gamma_{N-k+1} \leqslant 0, \quad \gamma_i > 0, \qquad i < N-k+1 \tag{4.4}$$

When all quantities $|\gamma_i| \sim 1$ (which, obviously, means that the wave propagation velocity is not close to any intermediate speed of sound), the first $k-1$ reactions may be considered to be in complete equilibrium. The flow region decomposes into $N-k+1$ zones. Solution in the first zone is determined by the course of the k- th reaction and is defined by Eq. (4.1) but, since in accordance with (4.4) $\gamma_{N-k+1} < 0$, we have here a completely dispersed wave. Hence integration of (4.1) necessitates the selection of initial values from the condition that v and q_k and their derivatives must tend to zero when $r \to -\infty$. It follows from (4.4) that in the remaining zones solutions are determined as in the case of a wave with partial dispersion considered above.

The singular nature of intermediate speeds of sound is revealed when one of the quantities $|\gamma_{N-k}| \ll 1$, which means that the propagation velocity in the steady solution is close to the intermediate speed α_{N-k}. In such wave the first $k-1$ reactions proceed steadily. The flow region may be divided into $N-k$ zones. In the first of these the flow is in the form of a completely dispersed wave, but the reactions numbered k and $k+1$ cannot be considered separately there. The flow in that region is defined by the equations

$$2(\varepsilon m_0 v - \varepsilon_a^2 \gamma_{N-k+1}) \frac{dv}{dr} = l\varepsilon_a^2 \left(e_k \frac{dq_k}{dr} + e_{k+1} \frac{dq_{k+1}}{dr} \right)$$

$$\frac{dq_k}{dr} = -L(\lambda_k q_k - e_k v), \quad \frac{dq_{k+1}}{dr} = -L(\lambda_{k+1} q_{k+1} - e_{k+1} v)$$

The analysis of remaining zones is a repetition of that in the case of a completely dispersed wave.

All conclusions about steady solutions obtained here by investigating the problem of piston can, obviously, be directly derived from the steady equations (1.1) and (1.2) with boundary conditions (2.3). Such analysis is, however, outside the scope of this paper.

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