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QUALITATIVE ANALYSIS OF UNSTEADY HEAT AND MASS TRANSFER MODES IN A BOUNDARY LAYER WITH CHEMICAL REACTIONS AND INTENSIVE INJECTIONS

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The effect of chemical reactions in the gas phase on unsteady heat and mass transfer in the neighborhood of the leading stagnation point of a streamlined body is investigated using the qualitative theory of dynamic systems. The necessary and sufficient conditions of uniqueness and stability of steady heat and mass transfer modes are formulated.

Processes of combustion and thermochemical disintegration of many gasifiable and volatile condensed substances occur in two stages [1 —3], the first of which is gasification with formation of intermediate gaseous chemically active products which in the second stage enter into gas phase chemical reactions. This is accompanied by intensive injection of gaseous products of thermochemical disintegration of the streamlined body surface.

Solution of the problem of intensive injection was investigated in [4 — 6] of which [4, 5] dealt with equations of the chemically frozen boundary layer, while [6] dealt with that of the chemically unstable one. In all of these papers the problem was treated in the steady formulation.

The aim of this paper is to provide a method for the approximate analytical investigation of the effect of gas phase reactions on the stability of steady heat and mass transfer modes and to obtain conditions of existence, uniqueness, and stability of steady solutions of the related boundary value problem.

1. Statement of the problem. The flow of heated gas in the neighborhood of the leading stagnation point of a gasifying body of revolution is considered. The chemically active gasification products A_g drawn in by the gas stream take part in the gas phase reaction in the body surface neighborhood, i. e. the chemical transformations run according to the scheme

$$A_s \rightleftarrows A_g \rightleftarrows B \tag{1.1}$$

where A_s is the initial condensed substance, B are the products of the gas phase reaction, and subscripts s and g denote the substance in the condensed and gaseous state, respectively. The gasification process is understood here in the meaning given to it in [7]. Evaporation and sublimation may be considered to be particular cases of that process.

The scheme (1.1) implies that both stages of thermochemical disintegration may be reversible. We assume below that if gasification (gas phase reaction) is endothermic, such as for example, sublimation (dissociation), it is reversible, and if it is exotermic, then it is irreversible.

It should be pointed out that for simplicity of subsequent exposition the kinetic scheme definition in the form (1.1) is based on the assumption that A_g is a gas of identical composition to that of the initial substance, as is the case of sublimation and evaporation of some condensed substances [1, 7]. If the gasification results in formation of several products of which only part participate in the gas phase reaction, scheme (1.1) is generally not valid. If, however, it is assumed that the gasification rate is restricted by any one of the intermediate components, and it is taken into account that the mass rate of that component formation due to the gasification reaction differs only by a constant factor from the gasification mass rate, the obtained below results can be extended to the case when A_g is not of identical chemical composition, as exampliefied by the gasification of gunpowder [2].

It is assumed that a strong injection of gasification products takes place, and that the known two-zone pattern of flow around the reacting body takes place. In that pattern the effect of viscous forces close to the body is negligibly small, and the boundary layer is separated from the body and formed in the neighborhood of the contact discontinuity that separates regions of inner and outer flows. The rate of the gas phase reaction is assumed to depend only on the temperature and concentration of the single restricting component of the gaseous mixture. The conditions of existence, uniqueness, and stability of steady modes of heat and mass transfer in the boundary layer are to be determined.

The problem thus formulated reduces to the determination of conditions of existence, uniqueness, and stability of steady solutions of the following boundary value problem expressed in dimensionless form:

$$f''' + ff'' = \beta_1 \left[(f')^2 - \frac{\rho_e}{\rho} \right], \quad \frac{\rho_e}{\rho} = \frac{1 + \beta\Theta}{1 + \beta\Theta_e} \frac{M_e}{M} \tag{1.2}$$

$$\frac{1}{\Pr} \Theta'' + f\Theta' = \frac{1}{\pi_t} \left[\frac{\partial\Theta}{\partial\tau} - \frac{\alpha_2}{\gamma} \pi_q \pi_\delta R_2 (C, \Theta) \right]$$

$$\frac{1}{\mathrm{Sc}} C'' + fC' = \frac{1}{\pi_t} \left[\frac{\partial C}{\partial\tau} + \pi_\delta R_2 (C, \Theta) \right]$$

$$\frac{\partial^2 \Theta_s}{\partial y_s^2} + \gamma \sqrt{\pi_x} \frac{\rho_w}{\rho_s} R_1 \frac{\partial\Theta_s}{\partial y_s} = \frac{\partial\Theta_s}{\partial\tau} \tag{1.3}$$

$$\frac{\lambda_w \rho_w}{\lambda_e \rho_e} \sqrt{\frac{\pi_t}{\Pr}} \left(\frac{\partial\Theta}{\partial\eta} \right)_w + \alpha_1 \frac{\rho_w}{\rho_e} R_1 - \tag{1.4}$$

$$\pi_\sigma [(1 + \beta\Theta_w)^4 - (1 + \beta\Theta_e)^4] = -K_e \left(\frac{\partial\Theta_s}{\partial y_s} \right)_w$$

$$-\frac{\lambda_w}{\lambda_e} L \sqrt{\frac{\pi_t}{\Pr}} \left(\frac{\partial C}{\partial\eta} \right)_w = \gamma R_1 (1 - C_w)$$

$$\Theta |_{\eta=0} = \Theta_s |_{y_s=0}, \quad \Theta_s |_{y_s \to \infty} \to -\Theta_{sH}$$

$$f |_{\eta=0} = f_w = -\frac{\gamma R_1}{\sqrt{\pi_t \Pr}} \frac{\rho_w}{\rho_e}, \quad \left(\frac{\partial f}{\partial\eta} \right)_{\eta=0} = 0$$

$$\tau = \frac{t}{t_*}, \quad t_* = \frac{2 y_*^2 \rho_e c_{pe}}{\lambda_e}, \quad y_* = \frac{\lambda_e R T_*^2}{\rho_e E_1 | q_1 | k_1} \exp \frac{E_1}{R T_*}$$

$$y_s = -\frac{y\sqrt{\pi_\varkappa}}{y_*}, \quad \pi_\varkappa = \frac{\lambda_e \rho_s c_{ps}}{\lambda_t \rho_e c_{pe}}, \quad \Theta = \frac{E_1}{RT_*^2}(T - T_*)$$

$$R_1 = \frac{(\rho v)_w}{\rho_w k_1}\exp\frac{E_1}{RT_*}, \quad \gamma = \frac{c_{pe} RT_*^2}{|q_1| E_1}, \quad \pi_t = t_* \beta_x$$

$$\beta_x = \left(\frac{du_e}{dx}\right)_{x=0}, \quad \pi_\sigma = \frac{\varepsilon\sigma T_*^2 y_* E_1}{R\lambda_e}, \quad K_\varepsilon = \sqrt{\pi_c \pi_\rho}$$

$$\pi_c = \frac{c_{ps}}{c_{pe}}, \; \pi_\rho = \frac{\rho_s \lambda_s}{\rho_e \lambda_e}, \; \beta = \frac{RT_*}{E_1}, \Theta_{sH} = \frac{E_1}{RT_*^2}(T_* - T_{sH})$$

$$L = \frac{\mathrm{Pr}}{\mathrm{Sc}}, \quad \mathrm{Pr} = \frac{\mu c_p}{\lambda}, \quad \mathrm{Sc} = \frac{\mu}{\rho D}, \quad \beta_1 = \frac{2\zeta}{u_e}\frac{du_e}{d\zeta}$$

$$\alpha_1 = \frac{q_1}{|q_1|}, \quad \alpha_2 = \frac{q_2}{|q_2|}, \quad \pi_q = \frac{|q_2|}{|q_1|}, \quad \pi_\delta = \frac{1}{2}\pi_t \,\mathrm{Dam}$$

$$\mathrm{Dam} = \frac{k_2}{\beta_x}\exp\left(-\frac{E_2}{RT_*}\right), \quad \eta = \frac{ru_e}{\sqrt{2\zeta}}\int_0^y \rho\, dy, \quad \zeta = \int_0^x \mu_e \rho_e u_e r^2\, dx$$

Here and above τ and y_s are the dimensionless time and coordinate; ζ and η are Dorodnitsyn's variables in Lees's form; f and Θ are dimensionless functions of current and temperature; C is the mass concentration of the restricting component; R_1 and R_2 are dimensionless rates of gasification and gas phase reactions, respectively; α_1, α_2, β, γ, Dam, π_t, π_c, π_ρ, π_δ, $\pi_\varkappa$, π_σ, K_ε, L, Pr, Sc, β_1, π_q are dimensionless parameters; x and y are coordinates of an orthogonal system attached to the separation boundary of media; r is the mean curvature radius of the body; u and v are gas velocity components; ρ is the density; c_p is the specific heat at constant pressure; μ is the dynamic viscosity; M is the molecular weight of the gas mixture; T is the temperature; D is the effective coefficient of diffusion; λ is the thermal conductivity coefficient; E_1, q_1, k_1, E_2, q_2, and k_2 are, respectively, the activation energy, the heat effect and preexponent of gasification reaction and of gas phase reaction; ε is the blackness coefficient; σ is the Stefan–Boltzmann constant; R is the universal gas constant; the prime denotes differentiation with respect to η, and indices s, H, e, w, and $*$ denote parameters of the gas phase, of the condensed phase at $y_s \to \infty$, of the gas phase on the outer side of the boundary layer, parameters at the media interface, and characteristic quantities, respectively.

Equations (1.2) which define the heat and mass transfer in the gas phase in the neighborhood of the leading stagnation point of the solid body were derived on the assumption that the gas is optically clear, that the Prandtl and Schmidt numbers and the product of density into viscosity are constant, the gas mixture is in effect binary [8], and that the specific heats of various components are constant and equal. As in [9 – 11], it was also assumed that the equations of continuity and motion are quasi-stationary. It was shown in [12] that this assumption can be taken as justified for a fairly wide range of flow parameter variation.

The terms which define energy and mass transfer induced by heat conduction and diffusion were left in (1.4) in the formulas for energy and mass at the media interface, since according to [6] the temperature and concentration gradients at that interphase are nonzero in the presence of gas phase reaction.

Since we aim here at a qualitative investigation of heat and mass transfer modes, we need not to specify initial conditions.

If radiation can be neglected, the streamlined body surface does not disintegrate $(R_1 = 0)$ and remains at constant temperature T_w, while a constant intensive injection of reactive gas occurs through the body surface. This injection induces in the boundary layer a nonequilibrium exotermic chemical reaction in which components of the external oncoming stream and of the injection stream take part. Because of this the boundary problem (1.2) — (1.4) is simplified and assumes the form

$$f''' + ff'' = \beta_1\left[(f')^2 - \frac{\rho_e}{\rho}\right], \quad \frac{\rho_e}{\rho} = \overline{T}\,\frac{M_e}{M} \tag{1.5}$$

$$\frac{1}{\mathrm{Pr}}\overline{T}'' + f\overline{T}' = C_1\frac{\partial \overline{T}}{\partial \tau} - C_1C_2m(C, \overline{T}) \equiv F(\eta, \tau) \tag{1.6}$$

$$\frac{1}{\mathrm{Sc}}C'' + fC' = C_1\frac{\partial C}{\partial \tau} + C_1m(C, \overline{T}) \equiv \Phi(\eta, \tau) \tag{1.7}$$

$$\eta = 0: \ f = f_w = \text{const}, \ f' = 0, \ \overline{T} = \overline{T}_w = \text{const}, \ C = C_w = \text{const} \tag{1.8}$$

$$\eta \to \infty: f' \to 1, \ \overline{T} \to 1, \ C \to C_e \tag{1.9}$$

$$\overline{T} = \frac{T}{T_e}, \quad C_1 = \frac{1}{\beta_x t_*}, \quad t_* = \frac{2\rho_e^{1-n}}{K}, \quad C_2 = \frac{q_2}{c_p T_e}$$

where $\overline{T}$ is the relative temperature; m is the dimensionless gas phase reaction rate; F and Φ are dimensionless functions; C_1 and C_2 are the first and second Damköhler dimensionless numbers of the gas phase reaction; n and K are the order and the coefficient of gas phase reaction rate at $T = T_e$, and the remaining notation was defined above.

The number of dimensionless criteria of similarity has been reduced in the formulation of the boundary value problem (1.5) — (1.9) by the use of new characteristic quantities.

2. Reduction of the boundary value problem (1.5) — (1.9) to a dynamic system. Let us first consider the flow around a nondisintegrating thermostat at intensive injection. It was shown in [4 — 6] that under intensive injections the flow in the boundary layer can be divided in two regions: an inner one $0 < \eta < \Delta$ ($\eta = \Delta$ is the coordinate of contact surface at which $f = 0$) in which the terms that define in Eqs. (1.5) — (1.7) the molecular transfer become unimportant, and the outer region $\Delta < \eta < \infty$ in which a fundamental change of boundary layer characteristics takes place. We shall consider Eqs. (1.5) — (1.7) in regions $0 < \eta < \Delta$ and $\Delta < \eta < \infty$ separately and stipulate the continuity of functions f, $\overline{T}$, and C and their derivatives with respect to η at the interface of these two regions.

Integrating twice Eqs. (1.6) and (1.7) with respect to η in region $\Delta < \eta < \infty$ using conditions (1.9) and obtaining an asymptotic estimate of the improper integrals as in [10], we obtain

$$f_\Delta'(1-\overline{T}_\Delta)-F(\Delta,\tau)=\sqrt{\frac{\pi}{2}\frac{f_\Delta'}{\mathrm{Pr}}}\,U_\Delta,\quad U=\frac{\partial\overline{T}}{\partial\eta} \tag{2.1}$$

$$f_\Delta'(C_e-C_\Delta)-\Phi(\Delta,\tau)=\sqrt{\frac{\pi}{2}\frac{f_\Delta'}{\mathrm{Sc}}}\,V_\Delta,\quad V=\frac{\partial C}{\partial\eta}$$

where the subscript Δ relates to parameters for $\eta = \Delta$.

According to [4 — 6] the quantities f''', $\overline{T}''$, C'' are negligibly small for intensive injections in the neighborhood of $\eta = 0$, hence for $0 < \eta < \Delta$ it is possible to consider that approximatley

$$f=f_w+f''(0)\frac{\eta^2}{2},\quad \overline{T}=\overline{T}_w+A\eta,\quad C=C_w+B\eta \tag{2.2}$$

$$\left(f''(0)=\frac{\beta_1\rho_e}{-f_w\rho_w}\right)$$

where A and B are functions of time. The expression for $f''(0)$ was obtained from Eq. (1.5) for $\eta = 0$ and boundary conditions (1.8). From (2.2) and conditions of joining at the contact surface we obtain

$$f_\Delta'=\frac{\rho_e}{\rho_w}\frac{\beta_1}{(-f_w)}\Delta,\quad U_\Delta=\frac{\overline{T}_\Delta-\overline{T}_w}{\Delta}=A,\quad V_\Delta=\frac{C_\Delta-C_w}{\Delta}=B \tag{2.3}$$

$$\Delta=-f_w\sqrt{\frac{2}{\beta_1}\frac{\rho_w}{\rho_e}}$$

The contact surface coordinates $\eta = \Delta$ calculated by the last of formulas (2.3) are the same as those calculated in [5] by the formula for $\eta = \Delta$, if the blunting is spherical ($\beta_1 = {}^1/_2$), and when it is cylindrical ($\beta_1 = 1$) these coordinates differ by 8%.

The substitution of (2.3) and the expressions for $F(\Delta, \tau)$, and $\Phi(\Delta, \tau)$ into (2.1) yields the following second order dynamic system (see the definition in [13]):

$$\frac{dC_\Delta}{d\tau}=-m_\Delta+\frac{1}{C_1}\left[a(C_e-C_\Delta)-L^{1/2}b(C_\Delta-C_w)\right]\equiv P(C_\Delta,\overline{T}_\Delta) \tag{2.4}$$

$$\frac{d\overline{T}_\Delta}{d\tau}=C_2m_\Delta+\frac{1}{C_1}\left[a(1-\overline{T}_\Delta)-b(\overline{T}_\Delta-\overline{T}_w)\right]=Q(C_\Delta,\overline{T}_\Delta)$$

$$a=\sqrt{2\beta_1\frac{\rho_e}{\rho_w}}>0,\quad b=\frac{1}{(-2f_w)}\sqrt{\frac{\pi a^3}{2\mathrm{Pr}}}>0,\quad m_\Delta\equiv m(C_\Delta,\overline{T}_\Delta)$$

If the chemical reaction is a first order irreversible one that conforms to the Arrhenius law, then functions m_Δ and parameter K are of the form

$$m_\Delta=C_\Delta\exp\left[\overline{E}\left(\frac{1}{\overline{T}_\Delta}\right)\right],\quad K=k_2\exp(-\overline{E}),\quad \overline{E}=\frac{E_2}{RT_e} \tag{2.5}$$

If the reaction is a reversible recombination reaction of air atoms, then according to [14] we have

$$m_\Delta=\frac{C_\Delta{}^2-C_{\Delta E}^2}{\overline{T}_\Delta^{3.5}(1+C_\Delta)},\quad C_{\Delta E}=C_E(\overline{T}_\Delta)=C_e\exp\left[C_3\left(1-\frac{1}{\overline{T}_\Delta}\right)\right] \tag{2.6}$$

where C_3 is a constant and the subscript E relates to atom concentration in the equilibrium state. In this case $K = 2K_1T_e^{-1.5}$ and $C_1 = K_1p_e^2T_e^{-3.5}R^{-2}\beta_x^{-1}$ where K_1 is the constant of the recombination rate and p_e is the pressure at infinity of the oncoming stream.

The qualitative analysis of the boundary value problem (1.5) — (1.9) thus reduces to the qualitative analysis of the dynamic system (2.4) which can be effected by the methods expounded in [13].

3. Analysis of the dynamic system (2.4) and physical interpretation of results. On the strength of the definition of C_Δ and $\bar{T}_\Delta$ the analysis can be restricted to the region of the phase plane C_Δ, $\bar{T}_\Delta$ of system (2.4), determined by the inequalities $0 < C_\Delta < 1,\ 0 < \bar{T}_\Delta < \infty$. Function m_Δ is assumed continuous in that region and to satisfy the conditions

$$\frac{\partial m_\Delta}{\partial C_\Delta} > 0, \quad \lim_{C_\Delta \to C_{\Delta E}} m_\Delta = 0, \quad \lim_{\bar{T}_\Delta \to \infty} m_\Delta = N < \infty \tag{3.1}$$

The first of these means that the chemical reaction has a positive order, the second indicates that in the equilibrium state the chemical reaction rate is zero (in the case of irreversible reaction $C_{\Delta E} = 0$), and the last condition implies the boundedness of the chemical reaction rate. It is obvious that, if function m_Δ satisfies Eqs. (2.5) and (2.6), conditions (3.1) are also satisfied.

The coordinates C_Δ° and $\bar{T}_\Delta^\circ$ of the equilibrium state of the dynamic system (2.4) are obtained from the system of equations $P(C_\Delta^\circ, \bar{T}_\Delta^\circ) = 0$, and $Q(C_\Delta^\circ, \bar{T}_\Delta^\circ) = 0$, which reduces to the form

$$\begin{gathered} C_\Delta^\circ = \frac{aC_e + L^{1/2}bC_w}{a + L^{1/2}b} + \frac{a(1 - T_\Delta^\circ) - b(T_\Delta^\circ - T_w)}{C_2(a + L^{1/2}b)} \\ C_1C_2m_\Delta^\circ = a(\bar{T}_\Delta^\circ - 1) + b(\bar{T}_\Delta^\circ - \bar{T}_w), \quad m_\Delta^\circ \equiv m(C_\Delta^\circ(\bar{T}_\Delta^\circ), \bar{T}_\Delta^\circ) \end{gathered} \tag{3.2}$$

The number of equilibrium states is equal to the number of roots of the second of Eqs. (3.2), and the stability and type of equilibrium states is determined by the signs of the following quantities:

$$\sigma_1 = \frac{\partial P}{\partial C_\Delta} + \frac{\partial Q}{\partial \bar{T}_\Delta}, \quad \Delta_1 = \frac{\partial P}{\partial C_\Delta}\frac{\partial Q}{\partial \bar{T}_\Delta} - \frac{\partial P}{\partial \bar{T}_\Delta}\frac{\partial Q}{\partial C_\Delta},$$

$$D_1 = \left(\frac{\partial P}{\partial C_\Delta} - \frac{\partial Q}{\partial \bar{T}_\Delta}\right)^2 + 4\frac{\partial P}{\partial \bar{T}_\Delta}\frac{\partial Q}{\partial C_\Delta}$$

calculated for $C_\Delta = C_\Delta^\circ$ and $\bar{T}_\Delta = \bar{T}_\Delta^\circ$. For the dynamic system (2.4) these quantities are

$$\begin{gathered} \sigma_1 = C_2\frac{\partial m_\Delta}{\partial \bar{T}_\Delta} - \frac{2a + (L^{1/2} + 1)b}{C_1} - \frac{\partial m_\Delta}{\partial C_\Delta} \\ \Delta_1 = -\frac{a + b}{C_1}\left(\frac{a + L^{1/2}b}{a + b}C_2\frac{\partial m_\Delta}{\partial \bar{T}_\Delta} - \frac{a + L^{1/2}b}{C_1} - \frac{\partial m_\Delta}{\partial C_\Delta}\right) \end{gathered} \tag{3.3}$$

$$D_1 = \left[C_1 \frac{\partial m_\Delta}{\partial \bar{T}_\Delta} + \frac{\partial m_\Delta}{\partial C_\Delta} + \frac{(L^{1/2} - 1) b}{C_1}\right]^2 - 4C_2 \frac{\partial m_\Delta}{\partial C_\Delta} \frac{\partial m_\Delta}{\partial \bar{T}_\Delta}$$

The analysis of relations (3.3) discloses important properties of system (2.4).

1°. If $\partial m_\Delta / \partial \bar{T}_\Delta \leqslant 0$, all equilibrium states of system (2.4) are stable nodes ($\sigma_1 < 0$, $\Delta_1 > 0$, $D_1 \geqslant 0$) and, according to Bendixon's criterion, limit cycles are absent [13].

2. if $\partial m_\Delta / \partial \bar{T}_\Delta > 0$, then for $L \geqslant 1$ all antisaddle points ($\Delta_1 > 0$) are stable ($\sigma_1 < 0$), and for $L < 1$ existence of unstable antisaddle points ($\Delta_1 > 0$, $\sigma_1 > 0$) is possible.

On the strength of (3.3) the equilibrium state of the dynamic system (2.4) is an unstable antisaddle, if for $C_\Delta = C_\Delta{}^\circ$ and $\bar{T}_\Delta \equiv \bar{T}_\Delta{}^\circ$ the condition

$$2a + (L^{1/2} + 1) b + C_1 \frac{\partial m_\Delta{}^\circ}{\partial C_\Delta{}^\circ} \equiv \alpha_1 < \alpha_2 \equiv C_1 C_2 \frac{\partial m_\Delta{}^\circ}{\partial \bar{T}_\Delta{}^\circ} < \alpha_3 \equiv \tag{3.4}$$
$$\frac{a + b}{a + L^{1/2} b} C_1 \frac{\partial m_\Delta{}^\circ}{\partial C_\Delta{}^\circ} + a + b$$

is satisfied. The double inequality (3.4) can be satisfied only when

$$\alpha_3 - \alpha_1 \equiv \frac{(1 - L^{1/2}) b}{a + L^{1/2} b} C_1 \frac{\partial m_\Delta{}^\circ}{\partial C_\Delta{}^\circ} - (a + L^{1/2} b) > 0 \tag{3.5}$$

which can only be satisfied for $L < 1$. If $L \geqslant 1$, then $\alpha_3 < \alpha_1$ and the inequality $\Delta_1 > 0$ leads to the condition $\sigma_1 < 0$.

3. If $\partial m_\Delta / \partial \bar{T}_\Delta > 0$ and $L < 1$, then (3.4) is the necessary and sufficient condition of existence of unstable antisaddle points, while the necessary condition of their existence is, by virtue of (3.5), of the form

$$C_1 > C_1{}^* \equiv \frac{(a + L^{1/2} b)^2}{(1 - L^{1/2}) b \, \partial m_\Delta{}^\circ / \partial C_\Delta{}^\circ} \tag{3.6}$$

Theorem 3.1. If function m_Δ satisfies conditions (3.1), where $C_{\Delta E} \equiv 0$, the following statements are valid:

1) the dynamic system (2.4) has an odd number of simple equilibrium states ($\Delta_1 \neq 0$) inside region G_1 determined by the inequalities $0 < C_\Delta < C_{\max}$ and $\bar{T}_{\min} < \bar{T}_\Delta < \bar{T}_\infty$, where $C_{\max}$ is the maximum of values C_w and C_e; $\bar{T}_{\min}$ is the minimum of values of $\bar{T}_w$ and $\bar{T}_e \equiv 1$, and $\bar{T}_\infty$ is a reasonably large quantity that exceeds $\bar{T}_w$ and 1, with the number of saddle points ($\Delta_1 < 0$) is smaller by one than the number of antisaddle points ($\Delta_1 > 0$);

2) The criterion of uniqueness of equilibrium state is of the form

$$\alpha_3 - \alpha_2 \equiv \frac{a + b}{a + L^{1/2} b} C_1 \frac{\partial m_\Delta{}^\circ}{\partial C_\Delta{}^\circ} + a + b - C_1 C_2 \frac{\partial m_\Delta{}^\circ}{\partial \bar{T}_\Delta{}^\circ} > 0 \tag{3.7}$$

Proof. It follows from (2.4) and (3.1) that nowhere outside region G_1 functions P and Q vanish, hence all equilibrium states of the dynamic system (2.4) lie within region G_1. Moreover, (2.4) and (3.1) imply the validity of inequalities

$$P(0,\bar T_\Delta)>0,\quad P(C_{\max},\bar T_\Delta)<0,\quad Q(C_\Delta,\bar T_{\min})>0,\quad Q(C_\Delta,\bar T_\infty)<0$$

Thus the rectangle bounding region G_1 contains all equilibrium states of the dynamic system (2.4) and is intersected by its phase trajectories entering it from outside (arrows in Fig. 1 indicate the direction of phase trajectories). In conformity with the Poincaré index theory [13] this implies the validity of the first statement of the theorem.

The second statement of the theorem follows from that in accordance with the first statement the dynamic system (2.4) has a saddle point then and only then when there exist several equilibrium states, while a unique equilibrium state occurs when condition $\Delta_1>0$ is satisfied for $C_\Delta=C_\Delta{}^\circ$ and $\bar T_\Delta=\bar T_\Delta{}^\circ$. On the strength of (3.3) and (3.4) the last condition implies condition (3.7). The theorem is proved.

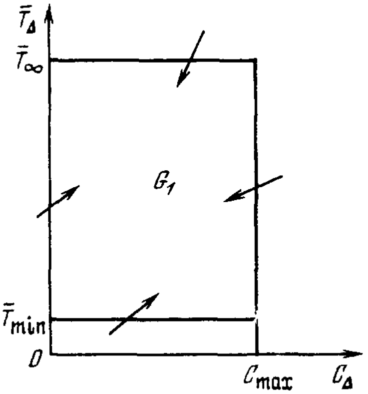

Fig.1

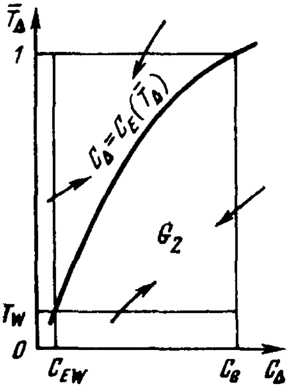

Fig.2

Theorem 3.2. If $\bar T_w<1$, $C_w<C_e$, and function m_Δ satisfies conditions (3.1), where $C_{\Delta E}=C_E(\bar T_\Delta)$ is a positive monotonically increasing function such that $C_E(\bar T_w)=C_{Ew}\leqslant 1$, and $C_E(1)=C_e$ (the curve of function $C_E(\bar T_\Delta)$ is shown diagrammatically in Fig. 2), then inside region G_2 defined by the inequalities $C_{Ew}<C_\Delta<C_e$ and $\bar T_w<\bar T_\Delta<1$ exists an odd number of simple equilibrium states of the dynamic system (2.4) with the number of saddle points smaller by one than the number of antisaddle points, and condition (3.7) is the criterion of uniqueness of equilibrium states.

Proof. Region G_2 is divided by the curve $C_\Delta=C_E(\bar T_\Delta)$ in two subregions (see Fig. 2): the upper one in which $C_{wE}<C_\Delta<C_{\Delta E}$ and by virtue of conditions (3.1) $m_\Delta<0$, and the lower in which $C_{\Delta E}<C_\Delta<C_e$ and $m_\Delta>0$. Taking this into account and using Eqs. (2.4), on the strength of conditions of the theorem we obtain that $P(C_{wE},\bar T_\Delta)>0$ for $\bar T_\Delta\geqslant\bar T_w$, $P(C_e,\bar T_\Delta)<0$ for $\bar T\leqslant 1$, $Q(C_\Delta,\bar T_w)>0$ for $C_\Delta\geqslant C_{wE}$, and $Q(C_\Delta,1)<0$ for $C_\Delta\leqslant C_e$. Hence the rectangle G_2 is intersected by phase trajectories of the dynamic system (2.4) entering it from outside. In accordance with the Poincaré index theory the region contains an odd number of simple equilibrium states in which the number of saddle points is smaller by one than the number of antisaddle points $(\Delta_1 > 0)$. Hence in accordance with (3.3) and (3.4) condition (3.7) is the criterion of uniqueness of equilibrium states inside region G_2 . The theorem is proved.

Corollaries. 1°. If function m_Δ is determined by formula (2.5), then by Theorem 3.1 all equilibrium states of the dynamic system (2.4) lie inside region G_1, and their uniqueness criterion (3.7) is of the form

$$C_1 \exp\left[E\left(1 - \frac{1}{\bar{T}_\Delta{}^\circ}\right)\right]\left[\frac{a+b}{a+L^{1/2}b} - \frac{EC_2C_\Delta{}^\circ}{(\bar{T}_\Delta{}^\circ)^2}\right] + a + b > 0 \qquad (3.8)$$

Since (3.2) implies that

$$\lim_{C_1\to 0} C_\Delta{}^\circ = \overset{\circ}{C}_{\Delta 0} = \frac{aC_e + L^{1/2}bC_w}{a + L^{1/2}b}, \quad \lim_{C_1\to 0} \bar{T}_\Delta{}^\circ = \overset{\circ}{\bar{T}}_{\Delta 0}\,\frac{a + b\bar{T}_w}{a+b}$$

$$\lim_{C_1\to\infty} C_\Delta{}^\circ = \overset{\circ}{C}_{\Delta\infty} = 0, \quad \lim_{C_1\to\infty} \bar{T}_\Delta{}^\circ = \overset{\circ}{\bar{T}}_{\Delta\infty} = \frac{a + b\bar{T}_w}{a+b} + C_2\,\frac{aC_e + L^{1/2}bC_w}{a+b}$$

hence in limit cases of a chemical reaction process when $C_1 \to 0$ and $C_1 \to \infty$ the uniqueness criterion (3.8) is satisfied and the dynamic system (2.4) has a single antisaddle point. Violation of condition (3.8) occurs only at intermediate values of the first Damköhler number $C_1 : 0 < C_{1,1} < C_1 < C_{1,2} < \infty$, if parameter $H = EC_2C_e \gg 1$. Bifurcation values $C_{1,1}$ and $C_{1,2}$ of parameter C_1 are determined by the equation $\alpha_2 = \alpha_3$, if the values of remaining parameters are fixed.

If in the considered case $L \geqslant 1$ or $L < 1$ and $C_1 \leqslant C_1{}^*$ (see formula (3.6)), the antisaddle points of the dynamic system are stable. For $L < 1$ and $C_1 > C_1{}^*$ the loss of antisaddle points stability and existence of unstable antisaddle points are possible when condition (3.4) is satisfied. In that case the loss of stability of the antisaddle point is accompanied by the generation of a stable limit cycle [13].

2°. If $\bar{T}_w < 1$, $C_w < C_e$, and function m_Δ satisfies Eq. (2.6) in which $C_3 \geqslant 1.75$ (according to [14] $C_3 = 4.022$), the dynamic system has in region G_2 a unique equilibrium state, viz. a stable node, and there are no limit cycles in that region.

In fact, for $C_3 \geqslant 1.75$ we have throughout the region

$$\frac{\partial m_\Delta}{\partial \bar{T}_\Delta} \equiv -\frac{3.5}{\bar{T}_\Delta^{4.5}(1 + C_\Delta)}\left[C_\Delta{}^2 + \left(\frac{C_3}{1.75\bar{T}_\Delta} - 1\right)C_{\Delta E}^2\right] < 0$$

Thus by virtue of Theorem 3.2, formulas (3.3), and conditions (3.7) imply that a unique equilibrium state, a stable node, exists in region G_2 in which according to Bendixon's criterion there are no limit cycles [13].

The above analysis shows the existence, uniqueness, and stability of the stationary mode and the absence of oscillating and self-oscillating heat and mass transfer modes in the case of flow past the leading point of a cold thermostat of dissociated air in the presence of intensive injection of an inert gas.

This conclusion is in agreement with the conclusion about the uniqueness of the mode of steady heat exchange between the thermostat leading point and the dissociated air stream arrived at in [15] on the basis of physical considerations, as well as with the numerical calculation results in [9].

The results presented in Sect. 4 according to which the dynamic system (2.4) in the case of Arrhenius dependence of reaction rate on temperature has for $L = 1$, $H \gg 1$, and $C_{1,1} < C_1 < C_{1,2}$ several equilibrium states, is in agreement with the results in [16, 17], where the numerical analysis of thermal interaction between the combustible mixture and an inert thermostat for $L = 1$ and $H \gg 1$ $(H = 432.7)$ in the absence of injection $(f_w = 0)$, as well as with injection of inert gas $(f_w = -0.15, -0.3, \text{and} -0.5)$ had shown the existence of two first Damköhler numbers which define the region of existence of three stationary solutions of the system of conservation equations. It was shown in [16, 17] that the critcial value of parameter C_1 corresponds to ignition and combustion extinction of mixture.

4. Reduction of the conjugate boundary value problem (1., 2)–(1. 4) to a dynamic system. Let us consider the case when gasification of a steamlined body with a spherically blunt nose $(\beta_1 = {}^1/_2)$ results in intensive injection of a chemically active gas. Double integration of Eq. (1.3) with respect to y_s with allowance for the first four boundary conditions (1.4) yields

$$K_s\left(\frac{\partial\Theta_s}{\partial y_s}\right)_w = \sqrt{\pi_t \,\mathrm{Pr}}\, \pi_c f_w \left[\Theta_w + \Theta_{sH} + \int_0^\infty J(y_s)\, dy_s\right] \tag{4.1}$$

$$I(y_s) = \exp\left(-\gamma\sqrt{\pi_\varkappa}\frac{\rho_w}{\rho_s}R_1 y_s\right)\int_0^{y_s}\frac{\partial\Theta_s}{\partial\tau}\exp\left(\gamma\sqrt{\pi_\varkappa}\frac{\rho_w}{\rho_s}R_1 y_s\right)dy_s$$

Substitution into the first of boundary conditions (1.4) of the expression for $(\partial\Theta / \partial\eta)_w$ derived from the third of Eqs. (1.2) in which in conformity with [4 – 6] we can set $\Theta'' = 0$ when $\eta = 0$ and the expressions (4.1) in which the improper integral has been calculated by the method described in [10], yields the equation

$$\begin{aligned} \frac{d\Theta_w}{d\tau} = Q_1(C_w, \Theta_w) \equiv \left[\left(1 + \pi_\rho\frac{\varphi_1}{\varphi_2}\right)\gamma\right]^{-1}\{\alpha_2\pi_q\pi_\delta R_2 + {} \\ \gamma^2\varphi_1 R_1\{[\alpha_1 - \gamma\pi_e(\Theta_w + \Theta_{sH})]\,\varphi_2 R_1 + {} \\ \pi_\sigma[(1 + \beta\Theta_e)^4 - (1 + \beta\Theta_w)^4]\}\} \\ \varphi_1 = \varphi_1(\Theta_w) = \frac{\lambda_e}{\lambda_w}, \quad \varphi_2 = \varphi_2(C_w, \Theta_w) = \frac{\rho_w}{\rho_e} \end{aligned} \tag{4.2}$$

The second equation is obtained from the second of conditions (1.4) by substituting in the latter the quantity $(\partial C / \partial\eta)_w$ obtained from the fourth of Eqs. (1.2) written for $\eta = 0$ in conformity with results in [4 – 6]

$$\frac{dC_w}{d\tau} = P_1(C_w, \Theta_w) \equiv -\pi_\delta R_2 + \gamma^2\varphi_1\varphi_2 R_1^2\,\frac{1 - C_w}{L} \tag{4.3}$$

5. Analysis of the dynamic system (4.2), (4.3) and physical interpretation of results. On physical considerations it is possible to restrict the analysis of the dynamic system (4.2) – (4.3) to that part of the phase plane C_w, Θ_w which satisfies the following conditions:

$$0 < C_w < 1,\ 0 < 1 + \beta\Theta_w < \infty,\ R_1(C_w, \Theta_w) > 0 \tag{5.1}$$

which are implied by the definition of β, C_w, and Θ_w and from the assumption of strong injection. By virtue of the definition of functions φ_1, φ_2, R_1, and R_2 the following conditions are satisfied:

$$\frac{\partial}{\partial C_w}(\varphi_2 R_1) \leqslant 0, \quad \frac{\partial}{\partial \Theta_w}(\varphi_2 R_1) > 0, \quad \frac{\partial}{\partial \Theta_w}(\varphi_2 R_2) > 0 \tag{5.2}$$

For simplicity we can assume $\varphi_1 = \sqrt{(1 + \beta\Theta_e) / (1 + \beta\Theta_w)}$. The dependence $\varphi_2 = \varphi_2(C_w, \Theta_w)$ is determined in conformity with (1.2). All parameters in Eqs. (4.2) and (4.3) are real and positive, except α_1 and α_2 which for exothermic and endothermic reactions are, respectively, equal plus and minus unity.

Theorem 5.1. If conditions

$$\alpha_2 = +1, \quad \lim_{C_w \to 0}(\varphi_2 R_2) = 0, \quad \frac{\partial}{\partial C_w}(\varphi_2 R_2) > 0 \tag{5.3}$$

are satisfied, then the following statements are valid:

1) the dynamic system (4.2), (4.3) has in the considered region (3.1) of the phase plane an odd number of simple equilibrium states with the number of saddle points smaller by one than the number of antisaddle points (nodes and focuses);

2) if all antisaddle points are unstable, at least one stable limit cycle which contains unstable equilibrium states exists in region (3.1).

Conditions (3.3) of the theorem have a simple physical meaning: the gas phase reaction is an irreversible exothermic reaction of positive order. Proof of this theorem is similar to that of Theorem 3.1.

The criterion of uniqueness and stability of steady modes and the conditions of existence of self-oscillation modes of heat and mass transfer with mild inducement follows from Theorem 5.1 and the existing correspondence between the signs of quantities similar to σ_1, Δ_1, and D_1 and the properties of the equilibrium states of system (4.2), (4.3). It is interesting that the necessary condition of existence of self-oscillating modes with mild inducement, of unstable steady modes, as well as oscillation modes of intensive thermochemical disintegration, obtained with the use of the indicated criteria, is of the form

$$\frac{\partial}{\partial \Theta_w} \ln\left(\frac{R_2}{R_1}\right) > 0 \tag{5.4}$$

When the dependence of functions R_1 and R_2 on Θ_w is exponential, condition (5.4) assumes the form $\pi_E = E_2 / E_1 > 1$.

The necessary condition (5.4) of existence of the self-oscillation mode suggests a possible physical mechanism of these. It is apparently similar to the mechanism of thermokinetic oscillations, which is described in [18] in connection with investigation of a two-stage reaction.

It is interesting to check conditions (5.4) on a few specific examples of thermochemical disintegration. In the case of intensive disintegration of the majority of heatproof (e.g., carbon-graphite sublimating) materials, when the quantity E_1 is fairly large ($E_1 \sim 170$ kcal/mole), condition (5.4) is not satisfied, hence the destabilizing effect of gas phase exotermic reactions on the process of thermochemical disintegration is not to be expected. A similar conclusion can be, apparently, made about the fast burning of ballistite H for which $\pi_E \sim 1$. The combustion of volatile explosives, such as nitroglycerin and nitroglycol (for the latter $\pi_E = 2.76$ [2]) may, on the contrary, result in the appearance of unsteady phenomena, including the transformation combustion into detonation.

REFERENCES

1. Beliaev, A. F., On the combustion of explosives. Zh. Fiz. Khim., Vol. 12, No. 1, 1938.

2. Zel'dovich, Ia., B., On the theory of combustion of powders and explosives. ZhETF, Vol. 12, No. 11 — 12, 1942.

3. Mills, A. F., The effect of gas phase chemical reactions on heat transfer to a charring ablator. J. Spacecraft and Rockets, Vol. 8, No. 6, 1971.

4. Kubota, T. and Fernandes, G., The boundary layer with considerable injection and heat transfer. Raketnaia Tekhnika i Kosmonavtika, No. 1, 1968.

5. Gershbein, E. A., On self-similar numerical and asymptotic solutions of boundary layer equations at considerable injections. Izv. Akad. Nauk, SSSR, MZhG, No. 3, 1971.

6. Zinchenko, V. I., Investigation of the effect of bulk chemical reactions on the characteristics of the laminar boundary layer flow at considerable injections: Collection: Mathematical Modelling of Aerothermochemical Phenomena. Moscow, Izd. VTs, Akad. Nauk, SSSR, 1974.

7. Dushin, Iu. A., Performance of Heatproof Materials in Hot Gas Streams. Moscow "Khimiia", 1968.

8. Tirskii, G. A., Calculating the effective diffusion coefficient in a laminar dissociated multicomponent boundary layer. PMM, Vol. 33, No. 1, 1969.

9. Agranat, V. M., Bertsun, V. N., Grishin, A. M., and Zinchenko, V. I., Statement and solution of some new conjugate problems of unsteady heat and mass transfer of reacting bodies in a stream of reactive gas. Collection: Heat and Mass Transfer —5, Vol. 2. Minsk, 1976.

10. Agranat, V. M. and Grishin, A. M., Qualitative investigation of unsteady combustion modes in the boundary layer. Collection: Numerical Methods of Continuous Medium Mechanics, Vol. 8, No. 5, Novosibirsk, SO Akad. Nauk, SSSR, 1977.

11. Winergardner, D. K. and Schmitz, R. H., Dynamics of heterogeneous reaction at a stagnation point. AIAA Journal, Vol. 5, No. 9, 1967.

12. Gilinskii, M. M., Unsteady modes of flow around a blunted body accompanied by strong injection of gas through the surface. Nauchn. Tr. Inst. Mekhaniki, No. 44, Izd. MGU, Moscow, 1976.

13. Bautin, N. N. and Leontovich, E. E., Methods and Procedures of Qualitative Investigation of Dynamic Systems in a Plane. Moscow, "Nauka", 1976.

14. Fay, J. A. and Riddell, F. R., Theory of stagnation point heat transfer in dissociated air. J. Aeronaut. Sci., Vol. 25, No. 2, 1958.

15. Chung, P. M., Fendell, F. E., and Holt, J.F., Nonequilibrium anomalies in the development of diffusion flames. AIAA Journal, Vol. 4, No.6.1966.

16. Alkidas, A. and Durbetaki, P., Staganation point heat transfer: the effect of the first Damköhler similarity parameter. Trans. ASME, Ser. C. J. Heat Transfer, Vol. 94, No. 4, 1972.

17. Durbetaki, P. and Hsu, H. W., Stagnation point heat transfer: ignition of a combustible mixture with inert gas injection through a porous wall. Trans. ASME, Ser. C. J. Heat Transfer, Vol. 97, No. 4, 1975.

18. Frank–Kamenetskii, D. A., Diffusion and Heat Transfer in Chemical Kinetics. Moscow, "Nauka", 1967.

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