SOME CHARACTERISTICS OF CHEMICAL REACTIONS IN VAPORIZING HYBRID SYSTEMS

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The author's method [1] of analyzing transport processes associated with the injection of a fuel-oxidizer mixture into a laminar boundary layer through a porous plate can be extended to the case of sublimation of a surface in a high-temperature gas flow. Such conditions may develop in hybrid (combined) systems in which a mixture of fuel and oxidizer from the vaporizing element must mix and react with an external oxidizer flow.

Preliminary results [2−4] indicate that in "pure" systems (in which oxidizer is not mixed with the solid propellant) the reaction kinetics have secondary significance as compared with the transport processes in the boundary layer and in the majority of cases can be ignored for all practical purposes. However, in other hybrid systems and, in particular, where a certain amount of oxidizer is mixed with the solid propellant, the reaction kinetics may acquire considerable importance. The methods of analyzing transport processes in hybrid systems proposed in [3,4], although they supplement one another, do not give a sufficient description.
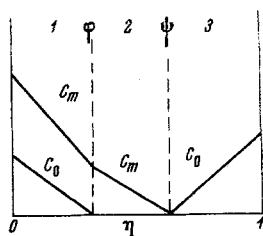
Distribution of concentrations, positions of reaction planes and reaction zones in the η coordinate system.

The present method of theoretical investigation of hybrid systems, although based on a diffusion interaction mechanism, permits a somewhat better understanding of the kinetic laws thanks to the assumption of two reaction fronts.

As shown in [1], this is conditioned by the fact that in the case of simultaneous vaporization of the fuel and oxidizer components the mixture temperature may reach the critical reaction temperature T^* (condition of formation of the first front) before complete stoichiometry is achieved. If the mass velocity of the fuel component is greater than the stoichiometric value corresponding to the presence of oxidizer in the mixture, the occurrence of a second reaction front will be determined by attainment of the full stoichiometric relation between the mass flow of fuel unreacted in the first front and the external oxidizer flow.

We will consider the problem of the laminar flow of a compressible gas (oxidizer) over a vaporizing flat plate with partial vapor pressure of the plate material in the free stream less than the saturated vapor pressure at the surface temperature; if the latter is less than the temperature at the triple point of the phase diagram, the plate material will vaporize, by-passing the liquid phase. We assume that the plate material is a hybrid system and vaporizes if the mass velocity of the fuel component is greater than the

stoichiometric value corresponding to the presence of oxidizer in the vaporizing mixture. In the boundary layer there are two reaction fronts (Fig. 1): $\varphi = \varphi(\eta)$ and $\psi = \psi(\eta)$.

As before, we assume that the chemical reaction rates considerably exceed the rate of diffusion of the components, as a result of which the chemical interaction is chiefly determined by diffusion of the components to the reaction planes, which we will treat as infinitely thin surfaces forming surfaces of discontinuity in the boundary layer. All the assumptions of boundary-layer theory are retained, the Prandtl number $N_{Pr} \neq 1 = $ const, the Schmidt number $N_{Sc} \neq 1 = $ const and $N_{Pr} \neq N_{Sc}$.

Since the mechanisms of the transport processes are similar for sublimation and injection, we will use the system of equations and boundary conditions for a laminar boundary layer presented in [1, 5]. The only difference is in the boundary conditions at the vaporizing hybrid surface in view of its self-regulating relationship with temperature and pressure.

We represent the concentration of fuel component at the surface of the plate in the form

$$C_{mw} = \frac{m_m}{m_w} \frac{p_{mw}}{p_\infty} , \tag{1}$$

where m_w is the molecular weight of the vaporizing binary mixture at the plate surface, which if $C_{mw} + C_{0w} = 1$ can be represented in terms of the concentration and the molecular weights of the components as follows:

$$m_w = \frac{m_m m_0}{m_m C_{mw} - m_0 (1 - C_{mw})} . \tag{2}$$

In the case of equilibrium vaporization the partial vapor pressure p_{mw} of the vaporizing material at the wall is equal to the partial saturated vapor pressure p^*_m at the wall temperature T_w, which for perfect gases and without allowance for the change in volume obeys the Clausius–Clapeyron law

$$\ln \frac{p_\infty}{p_{mw}} = -\frac{L}{R} \left(\frac{1}{T_w} - \frac{1}{T_s} \right) . \tag{3}$$

Here, T_s is the sublimation temperature.

Substituting the value of m_w from (2) into (1) and using (3), we obtain an expression for the concentration of the vaporizing fuel component at the surface of the plate in terms of the latent heat and the sublimation and plate surface temperatures:

$$C_{mw} = \left[1 + \frac{m_0}{m_m} (Z - 1) \right]^{-1} \times$$

$$\times \left(Z = \exp\left[\frac{L}{R} \left(\frac{1}{T_w} - \frac{1}{T_s} \right) \right] \right) . \tag{4}$$

We will show the applicability of (4) to gas systems that do not obey the perfect gas laws. With allowance for the change in volume, the Clausius-Clapeyron law takes the form:

$$L = T \frac{dp}{dT} V, \quad \text{or} \quad L = \frac{T}{p} \frac{dp}{dT} (RT - \alpha p)$$
$$\left(\alpha = \frac{RT}{p} - V \right). \tag{5}$$

Here, V is the change in volume during sublimation, and α is the deviation of the system from the ideal state.

In accordance with [6], we replace the partial pressures with the effective pressures f characterizing the tendency of the material to propagate between the inhomogeneous phases of the system, and using (5), we obtain

$$d \ln f = \frac{V \, dp}{RT} = \frac{L}{RT^2} dT. \tag{6}$$

After integration from T_S to T_W and correspondingly from f_{mw} to f_∞,

$$\ln \frac{f_\infty}{f_{mw}} = - \frac{L}{R} \left(\frac{1}{T_w} - \frac{1}{T_s} \right). \tag{7}$$

To obtain a unique determination of the position of the reaction fronts $\varphi = \varphi(\eta)$ and $\psi = \psi(\eta)$ and the concentration of the fuel component $C_{m\varphi}$ in the plane φ it is necessary to examine the combined diffusion-thermal problem.

When $\rho_0 \mu_0 = 1$ the equation of conservation of momentum is autonomous and the solution is given in [7].

For the region 1 between the wall surface and the reaction front φ (see the figure), for the vaporizing fuel component from the solution of the diffusion equation transformed to the form

$$C(\eta) = C_1 N_{Sc} \int_0^\eta \Phi(\eta, N_{Sc}) d\eta + C_2$$
$$\left(\Phi(\eta, N_{Sc}) = \left[\frac{K(\eta)}{K(0)} \right]^{N_{Sc}-1} \right), \tag{8}$$

with boundary conditions

$$C_{mw} = \left[1 + \frac{m_0}{m_m} (Z - 1) \right]^{-1} \quad \text{at} \quad \eta = 0,$$
$$C_m(\varphi) = C_{m\varphi} \quad \text{at} \quad \eta = \varphi, \tag{9}$$

we obtain an expression for the concentration distribution

$$C_m(\eta) = \left\{ C_{m\varphi} \int_0^\eta \Phi(\eta, N_{Sc}) d\eta + \left[1 + \frac{m_0}{m_m} (Z - 1) \right]^{-1} \times \right.$$
$$\left. \times \int_\eta^\varphi \Phi(\eta, N_{Sc}) d\eta \right\} \left\{ \int_0^\varphi \Phi(\eta, N_{Sc}) d\eta \right\}^{-1}. \tag{10}$$

Similarly, for the vaporizing oxidizer component from the solution of Eq. (8) with boundary conditions

$$C_{0w} = \frac{m_0}{m_m} (Z - 1) \left[1 + \frac{m_0}{m_m} (Z - 1) \right]^{-1}$$

at $\eta = 0$ and $C_0(\varphi) = 0$ at $\eta = \varphi$ (11)

we obtain the concentration distribution

$$C_0(\eta) = \frac{m_0}{m_m} (Z - 1) \left[1 + \frac{m_0}{m_m} (Z - 1) \right]^{-1} \times$$
$$\times \int_\eta^\varphi \Phi(\eta, N_{Sc}) d\eta \left\{ \int_0^\varphi \Phi(\eta, N_{Sc}) d\eta \right\}^{-1}. \tag{12}$$

The expressions for the distribution of fuel component concentration in region 2 (between the reaction fronts φ and ψ) and oxidizer concentration in region 3 (between the reaction front ψ and the outer edge of the boundary layer) coincide with those obtained in [1] and are, respectively, equal to

$$C_m(\eta) = C_{m\varphi} \int_\psi^\eta \Phi(\eta, N_{Sc}) d\eta \left\{ \int_\psi^\varphi \Phi(\eta, N_{Sc}) d\eta \right\}^{-1}, \tag{13}$$

$$C_0(\eta) = C_{0\infty} \int_\eta^\psi \Phi(\eta, N_{Sc}) d\eta \left\{ \int_1^\psi \Phi(\eta, N_{Sc}) d\eta \right\}^{-1}. \tag{14}$$

From the condition of mass balance in the φ plane for the mixture of vaporizing components we obtain expressions relating the quantities of interest φ, Ψ, $C_{m\varphi}$:

$$C_{m\varphi} \left[1 + \frac{m_0}{m_m} (Z - 1) \right] \int_0^\psi \Phi(\eta, N_{Sc}) d\eta =$$
$$= \left[1 - \frac{am_0}{m_m} (Z - 1) \right] \int_0^\varphi \Phi(\eta, N_{Sc}) d\eta. \tag{15}$$

It follows from the condition of mass balance of the fuel component and external oxidizer flow in the ψ plane that

$$C_{m\varphi} \int_1^\psi \Phi(\eta, N_{Sc}) d\eta = a C_{0\infty} \int_\psi^\varphi \Phi(\eta, N_{Sc}) d\eta. \tag{16}$$

Hence

$$C_{m\varphi} = a C_{0\infty} \int_\psi^\varphi \Phi(\eta, N_{Sc}) d\eta \left\{ \int_1^\psi \Phi(\eta, N_{Sc}) d\eta \right\}^{-1}. \tag{17}$$

After substituting (17) into (15) we can uniquely define the position of the reaction front ψ

$$a C_{0\infty} \left[1 + \frac{m_0}{m_m} (Z - 1) \right] \int_0^\psi \Phi(\eta, N_{Sc}) d\eta =$$
$$= \left[1 - \frac{am_0}{m_m} (Z - 1) \right] \int_1^\psi \Phi(\eta, N_{Sc}) d\eta, \tag{18}$$

or

$$a C_{0\infty} \left[1 + \frac{m_0}{m_m} (Z - 1) \right] R(0, \psi) =$$
$$= \left[1 - \frac{am_0}{m_m} (Z - 1) \right] R(1, \psi), \tag{19}$$

where, as in [1],

$$R(\eta_1, \eta_2) = \int_{\eta_1}^{\eta_2} \Phi(\eta, N_{Sc}) d\eta = \int_{\eta_1}^{\eta_2} \left[\frac{K(\eta)}{K(0)} \right]^{N_{Sc}-1} d\eta.$$

If $T_w > T^*$, the fuel-oxidizer mixture, vaporizing from the plate surface, reacts directly at the wall. After the chemical reaction the concentration of the fuel component at the wall

$$C_{mw} = \left[1 - \frac{am_0}{m_m}(Z-1)\right]\left[1 + \frac{m_0}{m_m}(Z-1)\right]^{-1}. \quad (20)$$

The solution of Eq. (8) with boundary conditions (20) and $C_m(\psi) = 0$ at $\eta = \psi$ leads to the following expression for the concentration distribution in the region between the surface of the wall and the reaction plane ψ:

$$C_m(\eta) = \left[1 - \frac{am_0}{m_m}(Z-1)\right]\left[1 + \frac{m_0}{m_m}(Z-1)\right]^{-1} \times$$
$$\times \int_\eta^\psi \Phi(\eta, N_{Sc})\, d\eta \left\{\int_0^\psi \Phi(\eta, N_{Sc})\, d\eta\right\}^{-1}. \quad (21)$$

Using the condition of mass balance in the plane ψ again leads to relation (19).

As follows from (15), it is not possible to determine φ and $C_{m\varphi}$ uniquely solely from the concentration conditions. For the unique determination of φ and $C_{m\varphi}$ it is also necessary to consider the thermal condition for the reaction plane φ following from the law of conservation of energy:

$$H_1' - H_2' = q\left(\frac{N_{Pr}}{N_{Sc}}\frac{dC}{d\eta}\right)_\varphi \quad \text{at} \quad \eta = \varphi. \quad (22)$$

The values of the enthalpies H_1 and H_2 are found from the solution of the energy equation in the form [5]

$$H'' - (N_{Pr} - 1)\left(\frac{K'}{K}\right)H' = u_\infty^2(1 - N_{Pr})\left(\frac{K'}{K}\eta + 1\right) \quad (23)$$

with boundary conditions

$$H(0) = H_w \quad \text{at} \quad \eta = 0, \qquad H = H_\infty \quad \text{at} \quad \eta = 1,$$
$$H_1 = H_2 = H_\varphi \quad \text{at} \quad \eta = \varphi,$$
$$H_2 = H_3 = H_\psi \quad \text{at} \quad \eta = \psi.$$

Correspondingly, for regions 1 and 2 we obtain for the enthalpies

$$H - H_w = u_\infty^2\left[\frac{\eta^2}{2} - N_{Pr}J(0, \eta)\right] +$$
$$+ \left\{H_\varphi - H_w - u_\infty^2\left[\frac{\varphi^2}{2} - N_{Pr}J(0, \varphi)\right]\right\}\frac{I(0, \eta)}{I(0, \varphi)}, \quad (24)$$

$$H - H_\varphi = u_\infty^2\left[\left(\frac{\eta^2}{2} - \frac{\varphi^2}{2}\right) - N_{Pr}J(\varphi, \eta)\right] +$$
$$+ \left\{H_\psi - H_\varphi - u_\infty^2\left[\left(\frac{\psi^2}{2} - \frac{\varphi^2}{2}\right) - \right.\right.$$
$$\left.\left. - N_{Pr}J(\varphi, \psi)\right]\right\}\frac{I(\varphi, \eta)}{I(\varphi, \psi)},$$

$$J(\eta_1, \eta_2) = \int_{\eta_1}^{\eta_2}\left[\frac{K(\eta)}{K(0)}\right]^\chi \int_{\eta_1}^{\eta_2}\left[\frac{K(\eta)}{K(0)}\right]^{-\chi} d\eta\, d\eta,$$

$$I(\eta_1, \eta_2) = \int_{\eta_1}^{\eta_2}\left[\frac{K(\eta)}{K(0)}\right]^\chi d\eta \qquad (\chi = N_{Pr} - 1). \quad (25)$$

The functions I, R, and J have been tabulated for various values of the N_{Pr} and N_{Sc} numbers and dis-

tributions of the function of the injection parameter $K(\eta)$ obtained from a solution analogous to the Blasius problem [7].

From condition (22), together with (10), (24), and (25), we obtain one more expression which, together with (15), enables us uniquely to define the values of the parameters φ and $C_{m\varphi}$:

$$\left\{H_\varphi - H_w - u_\infty^2\left[\frac{\varphi^2}{2} - N_{Pr}J(0, \varphi)\right]\right\}\frac{1}{I(0, \varphi)} -$$
$$- \left\{H_\psi - H_\varphi - u_\infty^2\left[\left(\frac{\psi^2}{2} - \frac{\varphi^2}{2}\right) - \right.\right.$$
$$\left.\left. - N_{Pr}J(\varphi, \psi)\right]\right\}\frac{1}{I(\varphi, \psi)} =$$
$$= q\frac{N_{Pr}}{N_{Sc}}\left\{C_{m\varphi} - \left[1 + \frac{m_0}{m_m}(Z-1)\right]^{-1}\right\}\frac{1}{R(0, \varphi)}. \quad (26)$$

We use the distribution of concentrations and enthalpies to determine the resulting effect on heat transfer. Since

$$\left(\frac{\partial H}{\partial y}\right)_{gw} = \left(\frac{\partial T}{\partial y}c_p + \sum_i h_i\frac{\partial C_i}{\partial y}\right)_{gw}, \quad (27)$$

$$\left(\frac{\partial T}{\partial y}c_p\right)_{gw} = \left(\frac{\partial H}{\partial y}\right)_{gw} - \left(\sum_i h_i\frac{\partial C_i}{\partial y}\right)_{gw}, \quad (28)$$

or, after conversion to the variable η, the quantity of heat supplied to the vaporizing surface

$$\left(\lambda\frac{\partial T}{\partial y}\right)_{gw} = \frac{\tau_w}{N_{Pr}}\left[\left(\frac{\partial H}{\partial \eta}\right)_{gw} - \left(\sum_i h_i\frac{\partial C_i}{\partial \eta}\right)_{gw}\right] \quad (29)$$

for a binary mixture

$$\left(\lambda\frac{\partial T}{\partial y}\right)_{gw} = \frac{\tau_w}{N_{Pr}}\left[\frac{\partial H}{\partial \eta} - \left(c_{pm}T\frac{\partial C_m}{\partial \eta} + c_{p0}T\frac{\partial C_0}{\partial \eta}\right)\right]_{gw} \quad (30)$$

substituting values of the concentration and enthalpy gradients from Eqs. (10), (12), and (24),

$$\left(\lambda\frac{\partial T}{\partial y}\right)_{gw} = \frac{\tau_w}{N_{Pr}}\left\{H_\varphi - H_w - \right.$$
$$\left. - u_\infty^2\left[\frac{\varphi^2}{2} - N_{Pr}J(0, \varphi)\right]\right\}\frac{1}{I(0, \varphi)} -$$
$$- \frac{\tau_w H_w}{N_{Pr}}\frac{aC_{0\infty}R(\varphi, 1)}{R(0, \varphi)R(1, \psi)}. \quad (31)$$

From the heat-balance equation for the vaporizing plate, the quantity of heat expended on heating the plate is

$$(\lambda\,\partial T/\partial y)_{sw} = (\lambda\,\partial T/\partial y)_{gw} - L(\rho v)_w \quad (32)$$

or, substituting (31) into (32),

$$\left(\lambda\frac{\partial T}{\partial y}\right)_{sw} = \frac{\tau_w}{N_{Pr}}\left\{H_\varphi - H_w - u_\infty^2\left[\frac{\varphi^2}{2} - \right.\right.$$
$$\left.\left. - N_{Pr}J(0, \varphi)\right]\right\}\frac{1}{I(0, \varphi)} -$$
$$- \frac{\tau_w H_w}{N_{Pr}}\frac{aC_{0\infty}R(\varphi, 1)}{R(0, \varphi)R(1, \psi)} - L(\rho v)_w. \quad (33)$$

Here, the third term on the right side of the equation takes into account the latent heat of sublimation. To determine the total mass flow of vaporizing components from the wall we use the Stefan formula [8],

taking into account the fact that the mixture is binary and the partial vapor pressure of the vaporizing substances at the surface is equal to the saturation pressure at the surface temperature

$$dp_m/dy = -vD^{-1}(P - p_m). \qquad (34)$$

But since for a binary mixture $D_m = D_0 = D = $ const and depends only slightly on concentration, after conversion to the variable $\eta = \eta(x, y)$

$$\frac{\tau}{\mu}\frac{dp_m}{d\eta} = -\frac{v}{D}(P - p_m) \qquad (35)$$

and, integrating, we finally obtain

$$\ln(P - p_m) = \frac{v}{D}\frac{\mu}{u_\infty \tau}\eta + C \qquad (36)$$

where C is a constant of integration. The total flow from the wall due to the "injection effect" is usually localized in the boundary layer, the conditions at the wall and at the outer edge of the boundary layer being

$$p_m = p_{mw} \quad \text{at} \quad \eta = 0, \qquad p_m = p_\infty = 0 \quad \text{at} \quad \eta = 1.$$

From the first of these conditions we find the constant of integration $C = \ln(P - p_{mw})$ and, after substituting into (36),

$$\ln\frac{P - p_m}{P - p_{mw}} = \frac{v}{D}\frac{\mu}{u_\infty \tau}\eta = \frac{(\rho v) N_{Sc}}{u_\infty \tau}\eta. \qquad (37)$$

From (37), using the second boundary condition, we find the value of the mass flow from the wall

$$(\rho v)_w = \frac{\tau_w u_\infty}{N_{Sc}}\ln\frac{Z}{Z - 1}. \qquad (38)$$

We substitute (38) into (33)

$$\left(\lambda\frac{\partial T}{\partial y}\right)_{sw} = \frac{\tau_w}{N_{Pr}}\left\{H_\varphi - H_w -\right.$$
$$\left. - u_\infty^2\left[\frac{\varphi^2}{2} - N_{Pr}J(0, \varphi)\right]\right\}\frac{1}{I(0, \varphi)} -$$
$$- \frac{\tau_w H_w}{N_{Pr}}\frac{aC_{0\infty}R(\varphi, 1)}{R(0, \varphi)R(1, \varphi)} - \frac{L\tau_w u_\infty}{N_{Sc}}\ln\frac{Z}{Z-1}. \qquad (39)$$

Equation (32) is valid if there are no chemical reactions at the wall. If $T_w > T^*$ and the vaporizing components react at the surface of the plate,

$$\left(\lambda\frac{\partial T}{\partial y}\right)_{sw} = \left(\lambda\frac{\partial T}{\partial y}\right)_{gw} - \sum\left(h_i\rho D\frac{\partial C}{\partial y}\right)_{gw} +$$
$$+ (\rho v H)_{sw} + q_{gw} - L(\rho v)_w. \qquad (40)$$

Here, we assume that the reaction proceeds with liberation of heat. Moreover, if we take into account radiation from the wall, we must add the extra term $\varepsilon\sigma T^4_w$ to the right side.

For a binary mixture

$$\left(\lambda\frac{\partial T}{\partial y}\right)_{sw} = \left(\lambda\frac{\partial T}{\partial y}\right)_{gw} -$$
$$- \left(h_m\rho_m D\frac{\partial C_m}{\partial y} + h_0\rho_0 D\frac{\partial C_0}{\partial y}\right)_{gw} +$$
$$+ H_w(\rho v)_w + q_{gw} - L(\rho v)_w, \qquad (41)$$

where h_{mw} and h_{0w} are the enthalpies of each of the components at the wall temperature.

Since from the mass balance condition we have

$$h_{1w}\rho_{1w}D\left(\frac{\partial C_1}{\partial y}\right)_w + h_{2w}\rho_{2w}D\left(\frac{\partial C_2}{\partial y}\right)_w =$$
$$= h_{1w}C_{1w}(\rho v)_w - h_{2w}(1 - C_{2w})(\rho v)_w,$$

then

$$\left(\lambda\frac{\partial T}{\partial y}\right)_{sw} = \left(\lambda\frac{\partial T}{\partial y}\right)_{gw} + (H_w - L)(\rho v)_w + q_{gw}. \qquad (42)$$

Substituting values of the concentration and enthalpy gradients from Eqs. (21) and (24) into (30), we determine the heat flow to the wall due to conduction

$$\left(\lambda\frac{\partial T}{\partial y}\right)_{gw} = \frac{\tau_w}{N_{Pr}}\left\{H_\psi - H_w -\right.$$
$$- u_\infty^2\left[\frac{\psi^2}{2} - N_{Pr}J(0, \psi)\right]\frac{1}{I(0, \psi)} -$$
$$- \frac{\tau_w H_w}{N_{Pr}}\left[\frac{am_0}{m_m}(Z - 1) - 1\right]\times$$
$$\left. \times\left[1 + \frac{m_0}{m_m}(Z - 1)\right]^{-1}\frac{1}{R(0, \psi)}\right. . \qquad (43)$$

With allowance for (43) the quantity of heat expanded on heating the vaporizing wall in the presence of a chemical reaction at its surface will be

$$\left(\lambda\frac{\partial T}{\partial y}\right)_{sw} = \frac{\tau_w}{N_{Pr}}\left\{H_\psi - H_w -\right.$$
$$- u_\infty^2\left[\frac{\psi^2}{2} - N_{Pr}J(0, \psi)\right]\frac{1}{I(0, \psi)} -$$
$$- \frac{\tau_w H_w}{N_{Pr}}\left[\frac{am_0}{m_m}(Z - 1) - 1\right]\times$$
$$\times\left[1 + \frac{m_0}{m_m}(Z - 1)\right]^{-1}\frac{1}{R(0, \psi)} +$$
$$+ \frac{(H_w - L)\tau_w u_\infty}{N_{Sc}}\ln\frac{Z}{Z-1} + q_{gw}. \qquad (44)$$

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