EFFECT OF THE RATE OF A HOMOGENEOUS CHEMICAL REACTION ON THE TEMPERATURE AND CONCENTRATION DISTRIBUTION IN THE BOUNDARY LAYER OF A TURBULENT GAS FLOW IN A CIRCULAR TUBE

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The authors examine a simplified model of a flowing binary gas mixture reacting at a finite rate. The factors determining the temperature distribution in the wall region are analyzed.

In analyzing heat transfer complicated by chemical reactions taking place in a moving medium it is most realistic to employ a hydrodynamic flow model using suitable laws of distribution of velocity and the turbulent coefficients of diffusion of heat, mass, and momentum.

At present, we lack a sufficiently reliable basis for applying to flows of chemically reacting gas mixtures the relations for the distribution of velocities and turbulent transport coefficients used in analyzing nonreacting gases.

This remark applies particularly to the viscous sublayer, in which phenomena associated with the release or absorption of heat and effects determined by changes in molecular structure can modify the hydrodynamic picture.

If it is postulated that in the turbulent core the heat and mass transfer potential gradients are equal to zero, the analysis can be considerably simplified by assuming that the variation of temperature, velocity, and concentration takes place in the wall region within the conditional thickness of the boundary layer.

In this case the deviation of the temperature and concentration distributions from linearity is determined only by the rate of the chemical reaction. This does not eliminate the mathematical difficulties, since in the radial direction the properties of the gas vary in accordance with the nonlinear character of the dependence of reaction rate on temperature and concentration. In order to overcome these difficulties attempts have been made to substitute for the actual dependence of the reaction rate a linear approximation [1,2]. Such linearization is possible only at small temperature drops between the wall and the gas. If the temperature drops are large, it is necessary to use only specific kinetic relations for the reaction rate. Moreover, we assume that the flow in the turbulent core is in chemical equilibrium at a temperature corresponding to the volume-averaged temperature.

In the wall region owing to diffusion the gas may be constantly in a state of chemical nonequilibrium even if the mass flux due to diffusion is stationary and the heat transfer processes steady. To exclude consideration of the problem in the axial direction, we introduce the assumption that the reaction rate is constant along the tube axis [1]. We will consider a gas mixture reacting according to the equation

$$aA \rightleftarrows bB. \tag{1}$$

The kinetic expression for the reaction rate is

$$r = K_{\mathrm{f}} P_A^a - K_{\mathrm{r}} \ P_B^b \tag{2}$$

or, taking into account the changes due to temperature,

$$r = K_{0\,\mathrm{f}} \exp\left[-\frac{E_1}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right] P^a Y_A^a - \\ - K_{0_{\mathrm{r}}} \exp\left[-\frac{E_2}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right] P^b Y_B^b. \tag{3}$$

We now write the energy equation for the hydrodynamic model adopted:

$$\frac{d}{dy}\left(\lambda_{\mathrm{fr}} \frac{dT}{dy} + J_A \Delta H\right) = 0. \tag{4}$$

By definition the reaction rate

$$r = \frac{dY_A}{dV} = -\frac{dJ_A}{dy}. \tag{5}$$

The diffusion flux J_A is determined from the generalized Fick's law:

$$J_A = -\rho D_{\mathrm{eff}} \frac{dY_A}{dy}. \tag{6}$$

In this case the effective diffusion coefficient is determined from the stoichiometry of the diffusion fluxes [3]:

$$D_{\mathrm{eff}} = \frac{D_{AB}}{1+\left(\frac{b}{a}-1\right) Y_A}. \tag{7}$$

Differentiating Eq. (6) and using relations (3), (4), and (7), we obtain, assuming ΔH fixed, the heat and mass transfer equations in dimensionless form:

$$\frac{d_2 \theta}{dz^2} = \frac{\bar{\tau}(\eta-1)}{k}\left\{\psi^a \exp\left[\frac{1}{\frac{1}{k_1 \theta}+\mu_1}\right] - \right. \\ \left. - \left(\frac{1-Y_{0A}\psi}{1-Y_{0A}}\right)^b \exp\left[\frac{1}{\frac{1}{k_2 \theta}+\mu_2}\right]\right\}, \tag{8}$$

$$\frac{d}{dz}\frac{\rho D_{\mathrm{eff}}}{\rho_0 D_{0\,\mathrm{eff}}}\frac{d\psi}{dz}=\bar{\tau}\left\{\psi^a \exp\left[\frac{1}{\frac{1}{k_1\theta}+\mu_1}\right]-\right.$$

$$\left.-\left(\frac{1-Y_{0A}\psi}{1-Y_{0A}}\right)^b \exp\left[\frac{1}{\frac{1}{k_2\theta}+\mu_2}\right]\right\}, \qquad (9)$$

where

$$\bar{\tau}=\frac{\tau_{\mathrm{dif}}}{\tau_{\mathrm{rel}}}=\frac{K_{0\mathrm{f}}P^a Y_{0A}^a\delta^2}{\rho_0 D_{0\mathrm{eff}}},\ \eta=1+\frac{2\rho_0 D_{\mathrm{eff}}\Delta H^2}{RT^2\lambda},$$

$$k=\frac{2\Delta H(T_{\mathrm{w}}-T_0)}{RT_0^2},\ k_1=\frac{E_1(T_{\mathrm{w}}-T_0)}{RT_0^2},$$

$$k_2=\frac{E_2(T_{\mathrm{w}}-T_0)}{RT_0^2},\quad \mu_1=\frac{RT_0}{E_1},\quad \mu_2=\frac{RT_0}{E_2},$$

$$z=\frac{y}{\delta},\quad \theta=\frac{T-T_0}{T_{\mathrm{w}}-T_0},\quad \psi=\frac{Y}{Y_0}. \qquad (10)$$

The boundary conditions are as follow:

$$\begin{aligned}&\text{at } z=0\ \ \theta=1,\ \frac{d\psi}{dz}=0,\\ &\text{at } z=1\ \ \theta=0,\ \psi=1.\end{aligned} \qquad (11)$$

From these results we obtain

$$\bar{q}=\frac{q}{q_{\mathrm{fr}}}=\frac{q}{\frac{\lambda_{\mathrm{fr}}(T_{\mathrm{w}}-T_0)}{\delta}}=-\left(\frac{d\theta}{dz}\right)_{z=0}, \qquad (12)$$

which characterizes the increase in the heat flux for a reacting mixture as compared with the flux calculated without allowance for the chemical reaction.

Equations (8) and (9) together with boundary conditions (11) were solved by a finite difference method on a computer for a mixture reacting according to the scheme 2A $\rightleftarrows$ 3B.

As a result, we obtained the dimensionless temperature and concentration profiles θ and ψ as a function of z (Fig. 1). Since the dimensionless complex $\bar{\tau}$ is the ratio of the diffusion time to the relaxation time and characterizes the departure from chemical equilibrium, as $\bar{\tau} \to 0$ the temperature profile becomes linear, $\bar{q} = 1$, which characterizes the "frozen" system. As $\bar{\tau} \to \infty$ the chemical relaxation rate becomes many times greater than the diffusion rate, and the system is in thermodynamic equilibrium. In this case the values of $\bar{q}$ reach a maximum.

To analyze the temperature distribution over the thickness of the layer δ, we obtained the dependence $dT/dy = f(y)$. It is clear from Fig. 2 that even at quite large values of the dimensionless complex $\bar{\tau}$ there are large changes in the temperature gradients at the wall. Using the data of the solution, for the case of an equilibrium reaction process we can estimate the distribution of thermal conductivity with allowance for the reaction component over the thickness δ (Fig. 3).

The distribution obtained shows that nonequilibrium conditions prevail in the thin boundary layers, while close to the wall there is a thin layer in which the chemical reaction does not affect heat transfer.

This is because remote from the wall energy is transported by heat conduction and diffusion. If the

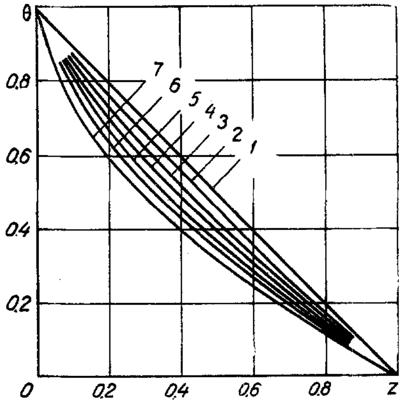

Fig. 1. Dimensionless temperature profiles for various τ and $\eta = 2$, $k = k_1 = 0.130$, $\mu_1 = 0.0495$, $E_2 = 0$: 1) without allowance for chemical reaction; 2) $\tau = 1$; 3) 10; 4) 50; 5) 100; 6) 300; 7) 500.

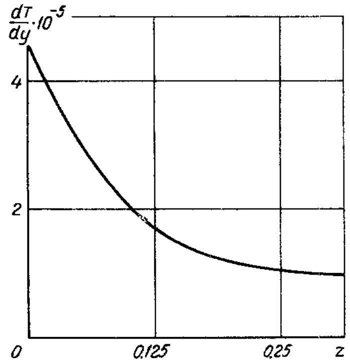

Fig. 2. Distribution of temperature gradient dT/dy (°C/M) over tube cross section z (m) at $\tau = 500$, $\eta = 3.97$ ($t_0 = 400°$ C, $t_{\mathrm{W}} = 450°$ C, P = 7 atm abs.).

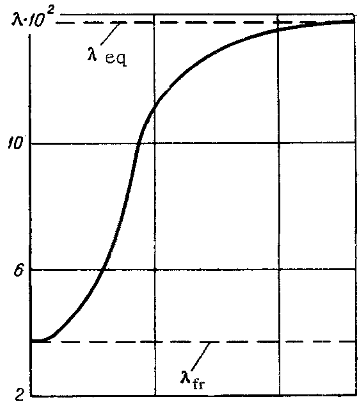

Fig. 3. Distribution of thermal conductivity λ (kcal/m · hr · deg) over tube cross section z (m).

wall is impermeable and is not a catalyst, in its immediate vicinity energy can be transported only by heat conduction. In the general case "frozen" boundary layers always occur when the boundary conditions are incompatible with chemical equilibrium. In this case, if at the wall $dY/dy = 0$, and there is an energy flux due to a distributed heat source, the temperature gradient at the wall is determined by the ratio of the quantity of energy transported by heat conduction and mass diffusion to the energy transported by heat conduction, i.e.,

$$-\frac{d\theta}{dz} = \frac{q_u}{q_{fr}} = \frac{q_{fr} - q_{dif}}{q_{fr}} = 1 + \frac{q_{dif}}{q_{fr}}. \quad (13)$$

We denote the ratio q_{dif}/q_{fr} by Q; then

$$-\frac{d\theta}{dz} = 1 + Q. \quad (14)$$

To determine Q we divide Eq. (8) by Eq. (9), assuming, for simplicity, that $\rho D_{eff}/\rho_0 D_{0eff} = 1$; as a result we obtain

$$\frac{d^2\psi}{dz^2} = \frac{d^2\theta}{dz^2}\,\frac{k}{(\eta - 1)Y_{0A}}. \quad (15)$$

As a result of the double integration of Eq. (15) we obtain the following relation for the dimensionless concentration:

$$\psi = \frac{Y_A}{Y_{0A}} =$$

$$\frac{k}{(\eta - 1)Y_0}\theta + \frac{k}{(\eta - 1)Y_0}\bar{q}z + 1 - \frac{k}{\eta - 1}\bar{q}. \quad (16)$$

At z = 0

$$\psi_w = \frac{Y_w}{Y_0} = 1 - \frac{k(\bar{q}Y_0 - 1)}{(\eta - 1)Y_0}. \quad (17)$$

From Eq. (17)

$$\bar{q} = \frac{(1 - \psi_w)(\eta - 1)Y_0}{k} + \frac{1}{Y_0}. \quad (18)$$

Substituting into this expression the values of the dimensionless complexes, we obtain

$$\bar{q} = \frac{\rho D_{eff}\Delta H(Y_0 - Y_w)}{\lambda_{fr}\ (T_w - T_0)} + 1. \quad (19)$$

Since $\bar{q} = d\theta/dz$,

$$Q = \frac{\rho D_{eff}\Delta H(Y_0 - Y_w)}{\lambda_{fr}\ (T_w - T_0)}. \quad (20)$$

In the case of an equilibrium reaction Y_w can be determined from the conditions of chemical equilibrium at the wall temperature; then

$$q_{eq.} = q_{fr} + \frac{\rho D_{eff}\Delta H(Y_0 - Y_w)}{\lambda_{fr}\ (T_w - T_0)}, \quad (21)$$

which makes it possible to estimate the maximum contribution of the chemical reaction to heat transfer.

Analysis shows that the contribution of the dissociation reaction is especially marked if Q > 9. At smaller Q the effect of the chemical reaction on heat transfer is, for practical purposes, small, especially if the departure from the equilibrium state is considerable, i.e., at small $\bar{\tau}$.

NOTATION

A and B are reactants and reaction products; *a* and b are stoichiometric coefficients; K_f and K_r are the rate constants of forward and reverse reactions; P_A is the partial pressure; P is the pressure; Y_A is the mole fraction of component; E is the activation energy; R is the gas constant; r is the reaction rate; T is the temperature; λ is the thermal conductivity; J_A is the diffusion flux; q is the heat flux; ΔH is the heat of reaction; ρ is the density of the mixture; D is the diffusion coefficient; δ is the conditional thickness of the boundary layer; y is the vertical coordinate. Subscripts: 0—parameters at volume-averaged temperature; w—parameters at wall temperature; fr—"frozen" value, i.e., without allowance for chemical reaction.

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