HEAT EXCHANGE DURING LAMINAR FLOW OF CHEMICALLY REACTIVE NO₂ GAS IN A FLAT TUBE WITH BOUNDARY CONDITIONS OF THE SECOND KIND

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UDC 536.244

The results of a calculation of heat exchange during the laminar flow of a chemically reactive gas in a flat tube are presented.

The problem of heat exchange during the laminar flow of liquids in tubes has obtained considerable development for liquids with constant and variable (monotonically changing) properties [1]. For chemically reactive gases reports are known in which heat exchange under conditions of chemical equilibrium is studied. In this case the chemical reaction is taken into account by means of "effective" thermophysical properties and the problem of heat exchange is reduced to the analogous problem for a chemically uniform gas with properties which are strongly dependent on the temperature. An extensive bibliograph on the study of heat exchange in these directions is presented in Petukhov's report [2].

At present not enough attention is paid to the effect of the chemical reaction rate on heat and mass transport during the laminar flow of a chemically reactive gas. A report can be mentioned [3] in which the problem of heat exchange during the laminar flow of a chemically reactive stream of $N_2O_4 \rightleftharpoons 2NO_2$ in a tube was solved numerically. The boundary conditions were assigned from the conditions that the wall temperature is constant and the concentration gradients of the mixture components at the wall are equal to zero. The results of the numerical calculation presented for different values of the rate constant indicate the considerable effect of the chemical reaction rate on the heat exchange.

We have studied the effect of the kinetics of the chemical reaction $2NO_2 \rightleftharpoons 2NO + O_2$ during the laminar flow of this system in a flat tube in the case of heating with boundary conditions of the second kind.

Let us examine the laminar flow of the chemically nonequilibrium gas $2NO_2 \rightleftharpoons 2NO + O_2$ in a heated flat tube in the boundary layer approximation with the following assumptions.

The gas flow is stationary and hydrodynamically stabilized, the gas is incompressible, its physical properties are constant (c_{pf}, λ_f, D_k, ρ, μ, Q_p), and the Lewis number Le = 1. At the entrance to the heated channel the temperature and concentrations of the gas components are constant over the cross section and the velocity profile is parabolic. The density of the heat flux q_w at the wall is assumed to be constant. The stoichiometric ratio $C_2/m_2 = C_3/2m_3$ exists between the concentrations of the components NO and O_2. The latter assumption simplifies the chemical reaction under consideration and reduces it to the type $2A \rightleftharpoons 3B$. With these assumptions we obtain a system of differential equations in dimensionless form:

$$\frac{3}{8}(1-Y^2)\frac{\partial \Theta}{\partial X} = \frac{\partial^2 \Theta}{\partial Y^2} - K, \tag{1}$$

$$\frac{3}{8}(1-Y^2)\frac{\partial C}{\partial X} = \frac{\partial^2 C}{\partial Y^2} + K. \tag{2}$$

Boundary conditions:

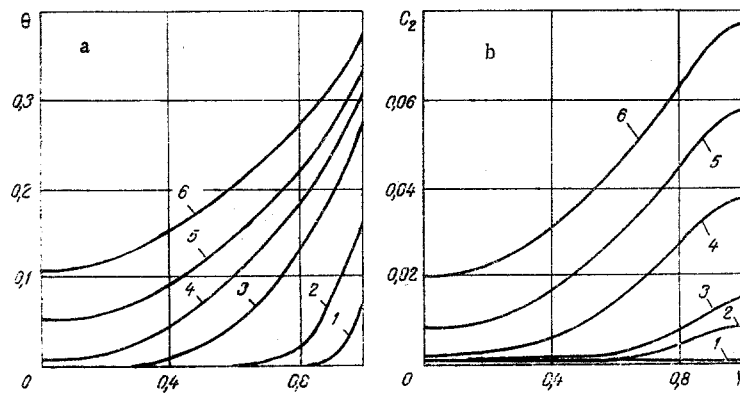$$X = 0, \quad 0 \leqslant Y \leqslant 1: \quad C = \Theta = 0;$$

Fig. 1. Distribution of temperature (a) and concentration of O_2 component (b) over radius of flat tube: 1) $X = 0.875 \cdot 10^{-4}$; 2) $0.875 \cdot 10^{-3}$; 3) $0.875 \cdot 10^{-2}$; 4) $2.63 \cdot 10^{-2}$; 5) $5.26 \cdot 10^{-2}$; 6) $8.75 \cdot 10^{-2}$.

$$X \geqslant 0, \quad Y = 0: \quad \frac{\partial C}{\partial Y} = \frac{\partial \Theta}{\partial Y} = 0;$$

$$X \geqslant 0, \quad Y_t = \pm 1: \quad \frac{\partial C}{\partial Y} = 0, \frac{\partial \Theta}{\partial Y} = 1.$$

(3)

Dimensionless complexes:

$$X = \frac{z}{h} \frac{1}{\text{Pe}}; \quad Y = \frac{y}{r_0}; \quad \Theta = \frac{T - T_0}{q_w r_0 / \lambda_f};$$

$$C = (C_2 - C_{20}) \frac{Q_p}{m_2 c_{pf}} \frac{\lambda_f}{q_w r_0}; \quad K = \frac{Q_p r_0 I_2}{m_2 q_w}.$$

The neglect of the term $\sum\limits_{k=1}^{3} q_k (\partial h_k / \partial Y)$ in Eq. (1) is a consequence of the assumption that the thermal effect of the chemical reaction is constant.

Using the equations

$$\sum_{k=1}^{3} q_k = 0; \quad q_3 = \frac{2m_3}{m_4} q_4,$$

we obtain

$$\sum_{k=1}^{3} q_k \frac{\partial h_k}{\partial Y} = \frac{q_2}{m_2} \frac{\partial Q_p}{\partial Y}.$$

The chemical reaction rate was determined from the following equations:

$$I = K_{c\partial} \left(\frac{C_1 \rho}{m_1} \right)^2 - 4 \frac{K_{c\partial}}{K_c} \left(\frac{C_2 \rho}{m_2} \right)^3;$$

(4)

$$I_2 = m_2 I; \quad C_1 = 1 - \frac{2m_1}{m_2} C_2; \quad K_c = \frac{K_p}{RT}.$$

The chemical reaction rate constant [4] and the equilibrium constant [5] are:

$$K_{c\partial} = 0.5 \cdot 10^{9.6} \exp\left(-26900/RT\right);$$

$$\ln K_p = -0.5845 \ln (T \cdot 10^{-4}) + 12.5862 \cdot 10^4 \frac{1}{T^2} - 147.088 \cdot 10^2 \frac{1}{T} + 17.5121 - 0.3079 \cdot 10^{-4} T$$

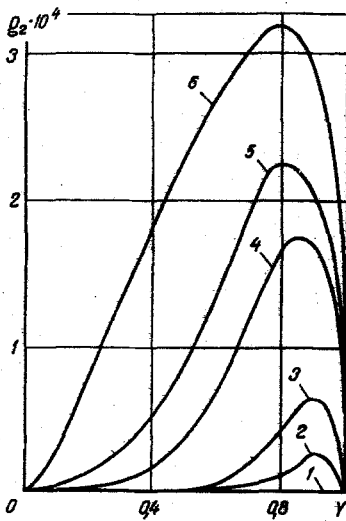$$- 1.6017 \cdot 10^{-8} T^2 - 0.1183 \cdot 10^{-12} T^3.$$

Fig. 2. Distribution of mass flow density of O_2 component over radius of flat tube: 1) X $= 0.788 \cdot 10^{-4}$; 2) $0.175 \cdot 10^{-2}$; 3) $0.35 \cdot 10^{-2}$; 4) $1.0 \cdot 10^{-2}$; 5) $1.75 \cdot 10^{-2}$; 6) $7.5 \cdot 10^{-2}$.

Besides the determination of the main characteristics of the chemically reactive stream calculations were also made of the average mass temperature

$$\bar{\Theta} = \int_0^1 \Theta \omega dY, \qquad (5)$$

the average mass concentration of the O_2 component

$$\bar{C} = \int_0^1 C \omega dY, \qquad (6)$$

and the average over the cross section of the mass source of the O_2 component

$$\bar{I}_2 = \int_0^1 I_2 dY. \qquad (7)$$

The parabolic type system of differential equations (1) and (2) in partial derivatives with the boundary conditions (3) was solved by the difference method on a Minsk-22 electronic computer. For the difference approximation an irregular grid is introduced with the steps

$$\Delta r_i = Y_i - Y_{i-1}; \quad i = 1, 2, \ldots, N,$$

$$\Delta x_j = x_{j+1} - x_j; \quad j = 0, 1, \ldots, M$$

and partition with respect to Y according to the equation

$$Y_i = \left(\frac{i-1}{N-1} \right)^b, \qquad (8)$$

where by setting the size of the step near the wall at $Y_N = 1$, $\Delta r_N = Y_N - Y_{N-1}$ one can find the exponent

$$b = \frac{\ln(1 - \Delta r_N)}{\ln \left(\frac{N-2}{N-1} \right)}. \qquad (9)$$

Using the implicit two-layer, six-point difference system of Crank and Nicolson the system of differential equations in partial derivatives (1), (2) was reduced to a system of nonlinear algebraic equations relative to the unknown functions C_{ij} and Θ_{ij} at the points $(Y_i; x_j)$:

$$A_1 C = B_1(C, \Theta); \quad A_2 \Theta = B_2(C, \Theta); \qquad (10)$$

where B_1, B_2, C, and Θ are vectors (grid functions); A_1 and A_2 are constant matrices (at the given j-th layer) of the three-diagonal type.

The approximation error of the equations and boundary conditions at the wall and at the axis has the order $O(\Delta x + \Delta Y)$. The system (10) was solved by the difference trial method with successive iterations at each layer $x = x_j$. For the choice of Δx and Δr systematic calculations were made for an inert gas with constant properties and estimates were made of the accuracy of the solutions. Comparisons were made with the results of an analytical solution [2] for the temperature profiles in the thermally stabilized section and from the values of the Nusselt numbers over the entire length of the channel studied, as well as from the thermal balance. The values $N = 51$ and $\Delta r_n = Y_n - Y_{N-1} = 0.007$ were chosen in our calculations from the condition of acceptable accuracy.

In addition, the step $\Delta r_1 = Y_1 - Y_0$ obtained from Eq. (8) was divided again at five nodes $(Y_k x_j)$ $k = 0$, $1, 2, \ldots, 6$. The initial step in x was equal to $\Delta x = 10^{-5}$. In the interval $10^{-4} \le x \le 10^{-3}$ the step was increased by an order of magnitude to $\Delta x = 10^{-4}$, and in the next interval $10^{-3} \le x \le 10^{-2}$ it was increased to $\Delta x = 10^{-3}$. To obtain a stable and sufficiently accurate solution this step was also kept for the case of $x \ge 10^{-2}$. With such a choice of the step Δx and Δr the error in calculating the temperature profiles did not exceed 4%, for the Nusselt numbers 1%, and for the heat balance 1%.

The distributions of temperature Θ, concentration of the O_2 component C_2, and mass flow density of the O_2 component over the radius of the tube are presented in Figs. 1, 2 for the following physical and geometrical characteristics:
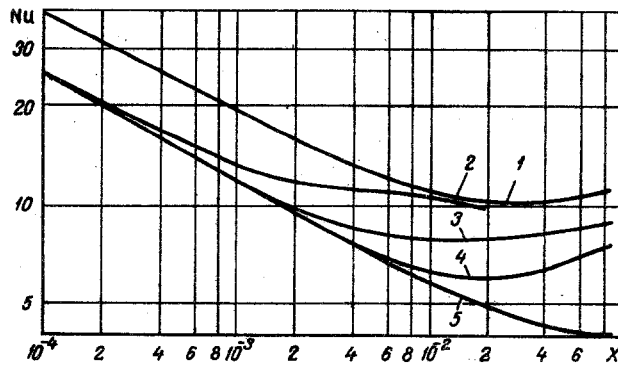
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Fig. 3. Variation in Nusselt number along length of flat tube: 1) chemical equilibrium stream; 2, 3, 4) nonequilibrium stream (2: Re = 57.2; 3: 181; 4: 572); 5) "frozen in" stream.

$a = \lambda_f / c_{pf}\rho = D_2 = 0.35 \cdot 10^{-5}$ m^2/sec; $\rho = 10$ kg/m^3; $m_1 = 46$ kg/kmole; $m_2 = 32$ kg/kmole; $c_{pf} = 10^3$ J/kg·deg; $Q_p = 1.135 \cdot 10^8$ J/kmole; $l = 0.00632$ m; $\overline{W} = 0.1$ m/sec; $T_0 = 500°$K; $C_{20} = 0.001$; $\partial T/\partial Y = q_w r_0 / \lambda_f = 595$ deg/m.

From Figs. 1, 2 it is seen how the growth of the thermal boundary layer, and along with it the diffusional boundary layer, occurs at the section of thermal stabilization in the region of small reduced lengths x < 0.03. The development of the profile of the mass flow density of the O$_2$ component, caused by the concentration diffusion $q_2 = (\rho D_2/r_0)(\partial C_2/\partial Y)$ (Fig. 2), depends both on the growth of the diffusional layer and on the kinetics of the chemical reaction.

An analysis of the results of the numerical calculation was conducted for the case of a change in the geometry of the flat tube and in the stream velocity averaged over the cross section, with the ratio between the dimensional and dimensionless length of the channel kept constant (X = 0.875 x). The values of the physical characteristics and the temperature gradient $(\partial T/\partial Y)_w$ at the wall were not changed.

In this case the profiles of the dimensionless enthalpy H and the dimensional enthalpy h for all the variants were unchanged and only the ratio between the enthalpy components for temperature and concentration varied:

$$H = \Theta + C = \frac{h - h_0}{c_{pf}} \frac{\lambda_f}{q_w r_0}; \qquad h - h_0 = c_{pf}(T - T_0) + \frac{Q_p}{m_2}(C_2 - C_{20}). \tag{11}$$

The calculation of the Nusselt number was determined from the equation

$$\text{Nu} = \frac{2}{\Theta_w - \overline{\Theta}}. \tag{12}$$

Distributions of Nusselt numbers along the length of the channel are presented in Fig. 3. The chemical reaction rate has a large effect on the variation in Nusselt numbers along the length of the channel. With an increase or decrease in the stream velocity the values of the Nusselt numbers approach the value for "frozen in" or chemical equilibrium streams. The chemical reaction rate has an analogous effect on the formation of the temperature and concentration profiles of the gas components.

Adding the differential equations (1) and (2), we obtain

$$\frac{3}{8}(1 - Y^2)\frac{\partial H}{\partial x} = \frac{\partial^2 H}{\partial Y^2}, \tag{13}$$

$$X = 0, \quad 0 \leqslant Y \leqslant 1: \quad H = 0,$$

$$X > 0, \quad Y = 0: \quad \frac{\partial H}{\partial Y} = 0,$$

$$X > 0, \quad Y = \pm 1: \quad \frac{\partial H}{\partial Y} = 1. \tag{14}$$

Equation (13) with the boundary conditions (14) is analogous to an energy equation describing the heat exchange during laminar flow of a chemically inert liquid with constant properties in a flat tube and with

boundary conditions of the second kind. Consequently the fields of dimensionless enthalpy H and dimensionless temperature Θ obtained through the solution of the appropriate equations (1), (2), and (13) will coincide:

$$H(X, Y) = \Theta_f(X, Y). \qquad (15)$$

The values of the average mass enthalpy and temperatures also coincide:

$$\bar{H}(X) = \bar{\Theta}_f(X). \qquad (16)$$

Therefore, for a chemically reactive gas the values of Nu_H, which relate to the difference of dimensionless enthalpies:

$$\text{Nu}_H = \frac{2}{H_w - \bar{H}} \qquad (17)$$

will coincide with the values of Nu_f.

Consequently,

$$\frac{\text{Nu}}{\text{Nu}_f} = \frac{H_w - \bar{H}}{\Theta_w - \bar{\Theta}} = \frac{h_w - \bar{h}}{c_{pf}(T_w - \bar{T})} . \qquad (18)$$

Let us define

$$\bar{c}_{pe} = \frac{h_w - \bar{h}}{T_w - \bar{T}} ,$$

then

$$\frac{\text{Nu}}{\text{Nu}_f} = \frac{\bar{c}_{pe}}{c_{pf}} . \qquad (19)$$

For a chemically equilibrium gas

$$\bar{c}_{pe} = \frac{1}{T_w - \bar{T}} \int_{\bar{T}}^{T_w} c_{pe} \, dT. \qquad (20)$$

For a mixture of NO_2 the maximum values are

$$\frac{\text{Nu}}{\text{Nu}_f} = \frac{\bar{c}_{pe}}{c_{pf}} \approx 3.$$

Equation (19) permits a rather direct calculation of the Nusselt number of a chemical equilibrium stream. For nonequilibrium streams one must know the difference in concentrations between the values at the wall and in the stream, which in turn requires that one find a criterial equation for the calculation of this difference.

NOTATION

$C_k = \rho_k / \rho$	is the relative concentration of k-th component;
ρ_k	is the partial density of k-th component;
$\rho = \sum_{k=1}^{n} \rho_k$	is the total density;
Q_p	is the calorific effect of reaction;
$K_{c\partial}$	is the dissociation rate constant;
K_c, K_p	are the equilibrium constants expressed through molar concentrations and partial pressures;
m_k, m	is the molecular weight of k-th component and of mixture;
I_k	is the mass sink or source of k-th component due to chemical reaction;
I	is the chemical reaction rate;
q_k	is the mass flow density of k-th component;
$w = 3(1-Y^2)/2$	is the dimensionless stream velocity. The remaining notation is standard.

Subscripts

1	shows that the value pertains to NO_2;
2	to O_2;

3	to NO;
0	to the channel entrance;
w	to the wall;
f	to a chemically inert gas.

LITERATURE CITED

1. V. D. Vilenskii, B. S. Petukhov, and B. E. Kharin, Teplofiz. Vys. Temp., 7, No. 5 (1969); ibid., 8, No. 4 (1970); ibid., 9, No. 3 (1971).
2. B. S. Petukhov, Heat Exchange and Resistance during Laminar Flow of Liquids in Tubes [in Russian], Énergiya, Moscow (1967).
3. R. J. Rothenberg and J. M. Smith, Canad. J. Chem. Engin., No. 4 (1966).
4. W. A. Rosser and H. Wise, J. Chem. Phys., 24, 493 (1956).
5. L. V. Gurvich and I. M. Rtishcheva, Teplofiz. Vys. Temp., No. 1 (1965).