SOME REGULARITIES OF HETEROGENEOUS REACTIONS IN LAMINAR FLOWS IN CHANNELS

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A gas-mixture flow in a channel on whose walls heterogeneous reactions take place is considered. Numerical simulation is performed on the basis of equations for a narrow channel. Results of a numerical solution of the equations are interpolated by a relation involving analytically obtained asymptotic formulas. Some regularities are obtained for the problem considered.

Gas flows in channels in the presence of chemical reactions are of great practical value for various problems of chemical engineering. These problems are usually solved numerically, but the results of the calculations, in contrast to theoretical solutions, do not make it possible to obtain general relations, and each new device requires an individual series of calculations. To find regularities it is reasonable to attempt to combine numerical and analytical methods [1], i.e., to use the first in obtaining generalizing material and the second (which usually are of an asymptotic character) in determining analytical relations by means of which numerical results are interpolated. The relations thus obtained possess many positive properties of analytical solutions, viz., simplicity, clear representation and generality, the possibility of employment in theoretical models (they can be integrated and differentiated), etc. Moreover, they differ only slightly from numerical solutions in accuracy. In what follows some regularities are obtained on the example of the problem (which is of a great practical interest) of a gas-mixture flow in a channel on whose walls heterogeneous reactions take place.

We consider a flow of a gas mixture containing the components A, B, the reaction product AB, and nonreacting components. We assume that an oxidizing reaction may occur on the wall $(\nu_A A + \nu_B B = \nu_{AB} AB)$; this is a one-stage process with some effective rate of the heterogeneous reaction W. The effective reaction rate is taken to mean the total amount of substance reacting per unit time on a unit free surface. In a first-order reaction, for a "monolithic" catalyst $W = KC$, and for a porous catalyst [2] $W = C(D'KS_v)^{1/2}$.

We write the formulation of the problem for a gas flow along a cylindrical channel with catalytic walls on the basis of equations for a narrow channel. Here a laminar mode is considered:

$$\frac{\partial \rho u y}{\partial x} + \frac{\partial \rho v y}{\partial y} = 0 , \tag{1}$$

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = -\frac{dp}{dx} + \frac{1}{y} \frac{\partial}{\partial y} (\mu y) \frac{\partial u}{\partial y} , \tag{2}$$

$$\rho u \frac{\partial h}{\partial x} + \rho v \frac{\partial h}{\partial y} = u \frac{dp}{dx} + \frac{1}{y} \frac{\partial}{\partial y} \left(\frac{\mu y}{\text{Pr}}\right) \frac{\partial h}{\partial y} + (\mu) \left(\frac{\partial u}{\partial y}\right)^2 + \sum_i \frac{\mu}{\text{Pr}} (\text{Le}_i - 1) h_i \frac{\partial C_i}{\partial y} , \tag{3}$$

$$\rho u \frac{\partial C_i}{\partial x} + \rho v \frac{\partial C_i}{\partial y} = \frac{1}{y} \frac{\partial}{\partial y} \rho y D_i \frac{\partial C_i}{\partial y} , \tag{4}$$

$$p = \rho R T / M . \tag{5}$$

The condition of conservation of the flow rate is

$$2\pi \int_0^y y\rho u \, dy = \text{const} . \tag{6}$$

The boundary conditions are:

on the axis of symmetry

$$\frac{\partial f}{\partial y} = 0 , \quad v = 0 ; \tag{7}$$

on the wall

$$\partial C_1 / \partial y = 0 \text{ for all components except } A, B, \text{ and } AB;$$

$$\frac{\partial C_i}{\partial y} = 0 \quad \text{for all components, except } A, B \text{ and } AB ;$$

$$\rho D_i \frac{\partial C_i}{\partial y} = -\omega_i \quad \text{for } A, B \text{ and the reaction product } AB ; \tag{8}$$

where

$$\omega_{AB} = -\nu_{AB} M_{AB} W/M ; \quad \omega_B = \nu_B M_B W/M ; \quad \omega_A = \nu_A M_A W/M , \tag{9}$$

and

$$T_w = \text{const} , \quad u_w = 0 . \tag{10}$$

Here

$$\text{Pr} = \frac{\mu c_p}{\lambda} , \quad \text{Le}_i = \rho D_i c_p / \lambda . \tag{11}$$

In the initial cross section the pressure, temperature, equal to the wall temperature, velocity profile (uniform or Poiseuille), and gas-mixture composition are taken to be constant. The mixtures $CO:O_2:N_2$ (with the heterogeneous reaction $CO + 1/2O_2 = CO_2$) and $H_2:O_2:N_2$ ($H_2 + 1/2O_2 = H_2O$) are considered as examples. Velocity profiles are assumed to be uniform or to correspond to a steady-state flow. Transport properties for the gas mixture are calculated by the Mason–Saxena and Wilkey formulas or the Stefan–Maxwell relations.

In a stationary process all substances should be carried by diffusion to the surfaces in amounts corresponding to stoichiometric equality of the flows. For both concentrations of reactants to vanish simultaneously on the wall, the condition of diffusive stoichiometry [2] should be fulfilled in a diffusion mode:

$$\frac{D_A \gamma_A}{\nu_A} = \frac{D_B \gamma_B}{\nu_B} = \frac{D_{AB} \gamma_{AB}}{\nu_{AB}} \tag{12}$$

in a motionless medium or in a steady-state mode,

$$\frac{D_A^{1-m} \gamma_A}{\nu_A} = \frac{D_B^{1-m} \gamma_B}{\nu_B} = \frac{D_{AB}^{1-m} \gamma_{AB}}{\nu_{AB}} \tag{13}$$

in the initial section of a moving medium. Here m is the exponent in the relation determining mass transfer: Nu $\sim \text{Re}^n \text{Pe}_d^m$. If equality (13) does not hold, then the rate of the process is determined by diffusion of the limiting component [2], for which the combination in expression (13) is the smallest (quantities relating to it will be denoted by the subscript lim).
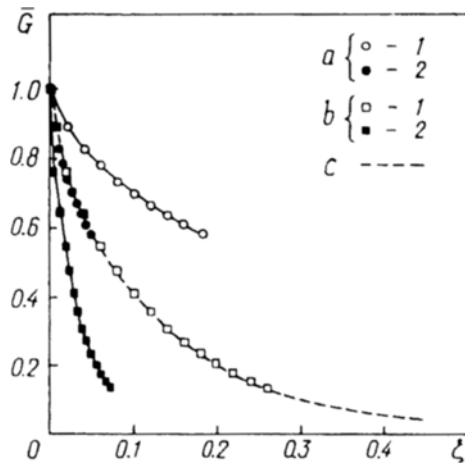
Fig. 1. Change in hydrogen flow rate depending on ζ for $\beta = \infty$ and a uniform initial profile of concentrations: a) the limiting component is hydrogen: 1) $\zeta(O_2)$, 2) $\zeta(H_2)$; b) the limiting component is oxygen: 1) $\zeta(O_2)$, 2) $\zeta(H_2)$; c) Le = 1.

Note that if the component with the smaller coefficient of diffusion is limiting, then it will remain such for the entire duration; if the component with the larger coefficient of diffusion is limiting, then at a certain ratio of concentrations and coefficients of diffusion a new limiting component is possible. Thus, on an absolutely catalytic wall (a diffusion mode) the concentration of the reactant I (A or B) for which the combination in expression (12) will have the smaller value will vanish and the boundary conditions on the wall will take the form

$$x_I = 0 , \tag{14}$$

and for the concentrations of the other components taking part in the reaction the condition of equality of the corresponding molar flows is laid down:

$$v_i j_i = v_I j_I . \tag{15}$$

We emphasize that conditions (14) and (15) are used only in the case of a diffusion mode (an absolutely catalytic wall).

The problem formulated was solved numerically.

DRe is the length scale for the equations used. In this situation it is natural to assume that the mass transfer characteristics can have a universal form when using $\zeta = x/D\mathrm{Pe}_{lim}$ as the coordinate, where $\mathrm{Pe}_{lim} = u_{mean}D/D_{lim}$.

We introduce a dimensionless flow rate of the component participating in the reaction:

$$\overline{G}_i (\zeta) = (G_i (\zeta) - G_{if})/(G_i (0) - G_{if}) , \tag{16}$$

where G_{if} is the flow rate of the component in an equilibrium mixture. If there is a deficit of the component in the initial mixture, then the expression takes a simpler form:

$$\overline{G}_i (\zeta) = G_i (\zeta)/G_i (0) . \tag{17}$$

The above considerations are confirmed by calculations conducted for both the components with close diffusion properties (Le$_{CO}$ ~0.9, Le$_{CO_2}$ ~0.7, Le$_{O_2}$ ~0.8, in the initial cross section a Poiseuille velocity profile is assigned with $u_{mean} = 0.5$ m/sec, $D = 2.5$ mm, $p = 100,000$ Pa, $T = 600$ K, the initial mass composition N$_2$:CO:O$_2$ = 95:3:2, uniform concentration profiles) and for the case of components with strongly differing diffusion properties (Le$_{H_2}$ ~3.2, Le$_{H_2O}$ ~1.1, Le$_{O_2}$ ~0.9, in the initial cross section a Poiseuille velocity profile is assumed with u_{mean} = 0.5 m/sec, $D = 2.5$ mm, $p = 100,000$ Pa; $T = 600$ K, the initial molar composition N$_2$:H$_2$:O$_2$ = 1:8:91 and N$_2$:H$_2$:O$_2$

= 43.9:41.9:14.2, uniform concentration profiles, Fig. 1). Calculations were conducted in the diffusion mode with the boundary conditions (14), (15). In the first case the product of the reaction CO_2 with the smallest coefficient of diffusion turned out to be the limiting component, and just this product should be used to calculate the self-similar coordinate. Figure 1 presents results for the case where the initial mixture has a stoichiometric excess of the component studied. (A mixture with the mass composition $N_2:H_2:O_2 = 47.5:41:11.5$, in which only 3% of the molar content of hydrogen can take part in the reaction, was considered as an example). Note that the hydrogen concentration on the wall has a value corresponding to a fully reacted mixture.

Thus, in processing the results an effective coefficient of diffusion of the limiting component should be used to calculate the Peclet number. In this case the results are closest to the self-similar curve corresponding to $Le_i = 1$. Calculations by the algorithm of [3] using the Wilkey formula and the Stefan−Maxwell relations for the coefficients of diffusion gave the same results with accuracy to the third decimal place for components with strongly differing properties (the molar content of hydrogen in the initial cross section varied from 1 to 14%).

Note that the steady-state velocity profile, in spite of the presence of chemical reactions and nonuniformity of concentration profiles, hardly differs from a Poiseuille parabola.

To consider these problems analytically a simplified formulation of the problem is usually employed, i.e., the velocity profile is regarded as parabolic and only one diffusion equation is written. The problem in such a formulation is solved, in principle, by the method of separation of variables; however, the result turns out to be very cumbersome, and a numerical method is used to find eigenvalues. Another way to solve this problem approximately is to use the Taylor model [4]. But it is shown in [5] that this model gives results that are less accurate the higher the rate of the chemical reactions, and for a diffusion mode the Taylor model is completely unsuitable. In [5] an approximate method is suggested that is appropriate for any rate of the chemical reactions. This is confirmed by comparison with numerical solutions. This method presupposes a Poiseuille velocity profile, a steady-state concentration profile, and first order of the reaction in concentration.

We write the system of equations [5] for the case under consideration for $Pe = \infty$, absence of a volumetric reaction, and the presence of a first-order heterogeneous reaction on the wall

$$\frac{1}{2} \frac{df_n}{d\zeta} + \left(1 - \frac{K_n}{2}\right) \frac{df_{n+1}}{d\zeta} - K_n \frac{df_{n+2}}{d\zeta} = 2n(n-1)f_{n-2} -$$

$$- 4n^2 \left(1 + \frac{K_n(n+1)}{2n}\right) + 4K_n(n+1)^2 f_n, \quad n = 0, 1, ..., N-1; \tag{18}$$

$$\frac{m-1}{2m} f_{m-2} - \left(1 + \frac{K_m(m+1)}{2m}\right) f_{m-1} + K_{m+1} \frac{(m+1)^2}{m^2} f_m = 0, \quad m = N, N+1. \tag{19}$$

Here N is the number of the approximation;

$$K_n = -2(4n + \beta)/(4 + 4n + \beta), \quad \beta = \omega R/(CD_{lim}); \tag{20}$$

C is the dimensionless concentration; ζ is the dimensionless coordinate; $f_n = 2\int_0^1 C_i(1/2 - \bar{y}^2)^n \bar{y} d\bar{y}$.

Note that the case where $\beta = \infty$ and f_0 is the mean concentration of component i reacting on the wall over the tube cross section corresponds to a diffusion mode. In what follows, analytical solutions that depend on coefficients $A(\beta)$, $B(\beta)$ that result from the solution of (18)-(20) are given.

In the first approximation

$$f_0 = \exp(-A(\beta)\zeta), \tag{21}$$

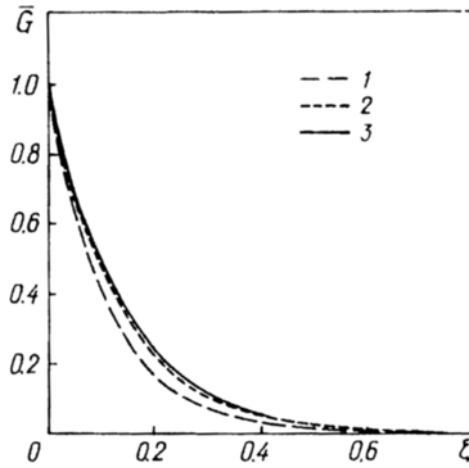where $A(\infty) = 9$ for a diffusion mode; in the second approximation

Fig. 2. Change in the relative flow rate of a reacting component depending on ζ (steady-state concentration profiles in the initial cross section): 1, 2) first and second approximations of the analytical method; 3) numerical solution, $\text{Le} = 1$.

$$f_0 = 0.9868 \exp\left(- A\,(\beta)\,\zeta\right) + 0.0132 \exp\left(- B\,(\beta)\,\zeta\right),$$

$$A\,(\infty) = 7.57, \quad B\,(\infty) = 112.6. \tag{22}$$

A comparison of analytical and numerical solutions for $\beta = \infty$ (for the numerical solution the cross section for which constant dimensionless concentration profiles $\overline{C} = C(y)/C$ ($y = 0$) are established is taken as the initial cross section) shows (Fig. 2) that in the second approximation the method of [5] gives satisfactory results and, consequently, it can be used sucessfully to calculate flows with chemical reactions on the wall in a section of a flow that is stationary in concentration profiles. In the case of a finite value of β for a first-order reaction the solution of (18)-(20) for $\beta > 100$ agrees with the asymptotic one corresponding to $\beta = \infty$ with an accuracy to 1%.

In practice, at the channel inlet there usually is a uniform velocity and concentration profile, and therefore, to obtain results suitable for use at the start of the channel one should take into account the effect of the initial flow section. The initial section is associated with growth of the boundary layer and transition to self-similar profiles.

We consider the processes at the start of the channel on the basis of boundary-layer theory, neglecting the longitudinal pressure gradient and considering the plane case (this obviously holds if the boundary layer thickness is much smaller than the tube radius). In the case where there are no volumetric reactions and $\text{Le}_i = 1$, it is obvious that there is a linear dependence between the velocity and concentration profiles.

Then, using the known solution for a plate by analogy with friction stress, we obtain the flow rate of the i-th component in the initial section

$$G_i \sim 1 - ax^{0.5}, \tag{23}$$

and the change in its flow rate in the main section, as was shown above, has an exponential character

$$G_i \sim \exp\left(- bx\right). \tag{24}$$

To describe completely the change in the flow rate along the entire tube length by computational data, we select an interpolation formula that describes asymptotically correctly the regularities at $\zeta = \infty$ and $\zeta = 0$. The dependences of the coefficients $A(\beta)$ for the first and second approximations, nondimensionalized by the value obtained at $\beta = \infty$, are retained with good accuracy in going from the first approximation to the second, thus making
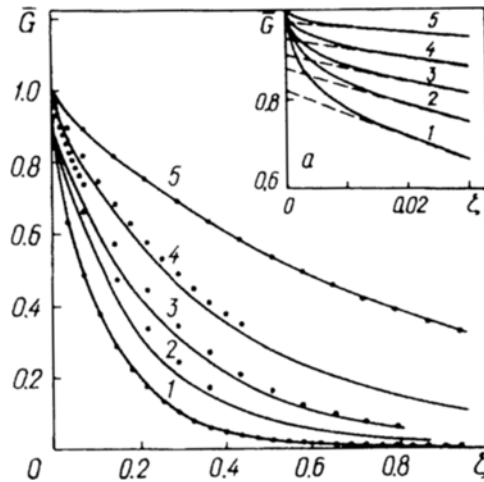
Fig. 3. Change in the relative flow rate of a reacting component depending on ζ in the case of uniform initial profiles of concentrations for various values of β: 1) ∞, 2) 4.23, 3) 2.12, 4) 1.7, 5) 0.42; points, numerical solution; solid curves (in the inset), formula (25); dashed curves, formula (26).

it possible to use the form of the dependence obtained in the first approximation to approximate the numerical solution by means of the corresponding scale multiplier. In the first approximation

$$A^1(\beta) = -4K_0/(0.5 + (1 - K_0/2) A_1 - K_0 A_2),$$

$$A_1 = (1 + K_1)/(4K_2), \quad A_2 = ((4 + 3K_2)(1 + K_1)/(4K_2) - 1)/(9K_3),$$

where the coefficients K_n are determined by relation (20). Then

$$A(\beta) = A(\infty) \delta(\beta), \quad \delta(\beta) = A^1(\beta)/A^1(\infty).$$

Having approximated the data resulting from the calculations and joined together the solutions (23), (24) by means of the transition frunction $\varphi(\zeta)$ so as to satisfy both regularities, we obtain the following form of $\overline{G}_i(\zeta)$:

$$\overline{G}_i(\zeta) = \exp\left\{ [-A(\beta) + 4.79\delta(\beta)\varphi(\zeta)]\zeta^{(1 - 0.5\varphi(\zeta))} - 0.195(1 - \varphi(\zeta))\delta(\beta) \right\}, \tag{25}$$

where $\varphi(\zeta) = (1 + 32\zeta)^{-5}$. For long tubes with ζ tending to infinity (25) passes over to

$$\overline{G}_I(\zeta) = \exp(-A(\beta)\zeta - 0.195\delta(\beta)), \tag{26}$$

where $A(\infty) = 7.28$, $\delta(\infty) = 1$ for a diffusion mode. Here we note that formula (26) describes well the flow along the entire section except for a small initial section. The convergence of (25) to (26) is presented in Fig. 3a. We emphasize that the relations obtained hold for a diffusion mode, whereas in a kinetic mode they hold only for the first order for the reaction.

The results of numerical and analytical calculations for a finite rate for the reaction ($\beta \neq \infty$) are also in satisfactory agreement.

Results of a numerical calculation for a flow for different β and a uniform initial concentration profile and results by (25) are given in Fig. 3 and are in good agreement. Note that in a kinetic mode with a reaction order different from unity the results should depend on the initial concentration.

The formulation of the problem of mass transfer for one of the components for $C_w = 0$ coincides with the well-known problem of heat transfer in a tube with a constant wall temperature, which is solved by the method of separation of variables. The solution is obtained in the form of an infinite series [6]; here, starting with some value

of the reduced length, the profiles of dimensionless temperature become self-similar, and all terms of the series, except the first, can be neglected. The solution takes the form

$$\frac{T - T_w}{T_0 - T_w} = T_* (\bar{r}) \exp \left(- 2\varepsilon^2 \frac{1}{Pe} \frac{x}{D} \right) , \quad \varepsilon^2 = 2Nu_\infty ,$$

where Nu_∞ is the critical Nusselt number (of the self-similar mode), $Nu_\infty = \alpha_\infty D/\lambda = 3.66$.

We introduce the diffusion Nusselt number $Nu_d = \alpha_d D/D_{lim}$, $\alpha_d = j_d/|C_w - C_0|$. It follows from the solution obtained that $Nu_d = A(\beta)/2$. Note that for a steady-state section the resulting Nusselt number is equal to 3.64, which differs only slightly from the value given above that was obtained from an analytical solution. The divergence that occurs is probably related to rounding-off errors in discarding terms of the series and errors in the numerical solution and the approximation.

On the basis of the regularities obtained we write a formula for determining the length of the catalytic channel that is needed to burn up the investigated component in the case where the initial section is small relative to the total channel length. We transform (26) to the form

$$C_i (x) = C_i (0) \exp (- A (\beta) \zeta - 0.195\delta (\beta)) ,$$

here C_i is the mean-flow-rate concentration of the i-th component.

We consider not only a single channel but also a block of channels. We rewrite the coordinate as $\zeta = x/x_*$, where the characteristic length x_* can be represented in the form

$$x_* = DPe_{lim} = (4RGT)/(\pi MpD_{lim}) = (4RG_sT)/(\pi MpD_{lim}N) ,$$

here G_s is the total flow rate through all channels of the block, N is the number of channels. Prescribing the required concentration $C(x)$ after passing the catalytic channel, we obtain

$$x = - x_* (0.195\delta (\beta) + \ln (C (x)/C (0)))/A (\beta) ,$$

whence it follows that the channel length is minimum in a diffusion mode for which the following conclusions hold:

 – with maintenance of the mass flow rate and the wall temperature the necessary length of the block is independent of the working mixture pressure (since $D_{lim} \sim 1/p$);

 – with maintenance of the mass flow rate through a single tube and the wall temperature the necessary length is independent of the tube diameter;

 – with maintenance of the mass flow rate through a block the necessary length of the catalytic block varries in inverse proportion to the number of channels;

 – with a fixed number of channels the block length is proportional to the square of the diameter of the channels.

On the basis of the regularity obtained we consider the problem of the power efficiency of catalytic-reactor operation. The power of surface forces applied to gas in a tube is $N_p = \Delta puS$, where S is the tube cross-sectional area.

We introduce the quantity $E = (G_{l0} - G_l)/N_p$ characterizing the power efficiency of catalytic-reactor operation. Then, using the above expressions for N_p, G_l, and the mass flow rate per second for Poiseuille flow, we obtain

$$E = C_{l0} (1 - \exp (- A (\beta) \zeta - 0.195\delta (\beta)))/(32u_{mean}^2 \zeta Pr) .$$

Note that the function $(1 - \exp (-A(\beta)\zeta - 0.195\delta(\beta)))/\zeta$ is a monotonically decreasing function of ζ, i.e., the efficiency of the channel decreases with its length.

By analogy with heat transfer and mass transfer, to reduce weight and size characteristics and to improve power characteristics the same measures can be employed as for enhancement of heat transfer. However, one should bear in mind that by virtue of the usual analogy between heat transfer and friction this will result in pressure losses.

We emphasize that the obtained results refer to the case of stationary processes under certain thermal conditions (T_w = const) with a negligible effect from gravity forces.

In general the results of the work indicate the possibility of generalizing the laws governing laminar flows of various gas mixtures in tubes with heterogeneous reactions at least under the conditions considered (first order for the reaction, constant wall temperature).

NOTATION

x, y, cylindrical coordinates; u, v, velocity components; u_{mean}, mean velocity over a cross section; C_i, mass concentration of the i-th component; C_p, heat capacity of the mixture; D', coefficient of diffusion in a porous material; D_i, coefficient of diffusion; D, channel diameter; $G_i(\zeta)$, flow rate of the i-th component; G_f, flow rate after completion of the reaction; h, enthalpy of the mixture; K, rate constant of the heterogeneous reaction; M, molecular weight; p, pressure; Pe, Peclet number; S_v, specific surface of the porous catalyst; T, temperature; W, rate of the heterogeneous reaction; γ, molar concentration; μ, dynamic viscosity; ν, stoichiometric coefficient; ρ, density; $\zeta = x/(D\text{Pe}_{lim})$.

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