DIFFUSION IN AN INHOMOGENEOUS VELOCITY FIELD IN THE PRESENCE OF A FIRST-ORDER HOMOGENEOUS CHEMICAL REACTION

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Upon taking the average of the local transport equation with a homogeneous first-order chemical reaction, a differential equation is obtained for the mean concentration over the channel section in the form of an infinite asymptotic series. Estimates are executed showing that we can limit ourselves to terms of third order or even second order for not-too-high reaction rates in the averaged transport equation; however, additional convective and source-like terms appear here in the equations. The theory is confirmed by an experiment in a 3.4-m operating chemical reactor.

The problem of determining the macrokinetic (effective) characteristics of a system (the diffusion, heat conductivity, electrical conductivity, etc.) on the basis of information about the local conductivity field configurations is of great theoretical interest and extreme practical importance.

Since the local characteristics of the medium are unknown in the general case, the local conductivity field can be considered random. The effective conductivity (for concreteness we later examine the diffusion process) should here depend on all the parameters governing the local diffusion random field, on all its moments, e.g., and therefore sufficiently universal formulas for the determination of the average field characteristics should have a quite complex structure.

Under certain simplifying assumptions (constancy of the mean concentration gradient over the channel length) satisfied with sufficient accuracy for practical purposes at just an extremely large distance from the source ($\mathrm{Pe}_r = \langle u\rangle R^2/(HD_r) \ll 7$), the equation for the effective conductivity, and consequently, the macroscopic (averaged) diffusion equation was obtained in [1-3] for a known (laminar or turbulent) fluid velocity profile in the absence of concentration sources (sinks).

The works by Taylor stimulated many publications of mainly experimental nature, where the principal condition of applicability of the model, the sufficiently long length (height) of the channel (apparatus) H for which the concentration gradient could be considered constant, was not sustained in the absolute majority of these papers. Consequently, the values found experimentally for the effective diffusion coefficient depended on the diameter and height of the apparatus, the physical properties of the mixtures investigated, the presence or absence of a chemical reaction, etc., whereupon the coefficient found in the tests could not be considered a parameter of the problem and its practical utilization turned out to be impossible in the majority of cases.

The self-consistent field theory [4-9] was used for the analysis of the effective characteristics in many papers. Comparison of the results of a computation by this method with experiment and independent direct computations by the Monte-Carlo method [7] showed its extremely high accuracy. Unfortunately, a computation by this method is successful only when taking into account specific features of the problem and neglecting factors not essential in the particular case under consideration.

Examination of the problem in a complete formulation is possible by applying the perturbation method. Selecting an appropriate "unperturbed" problem, the solution can be written in the form of a certain parameter, a perturbation treated sufficiently broadly at the present time.

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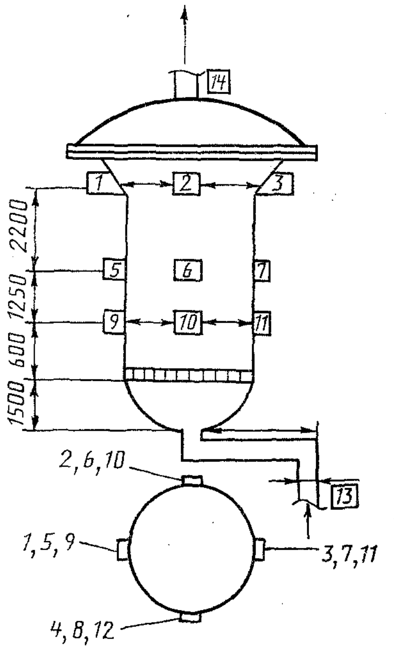

Fig. 1

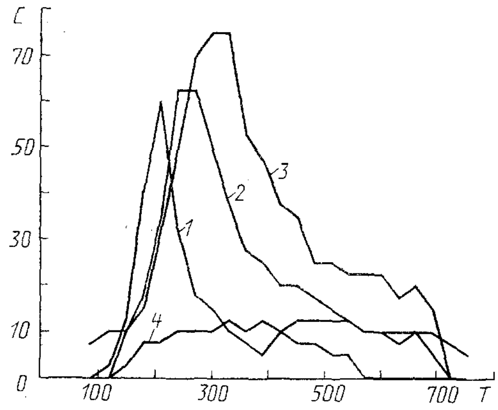

Fig. 2

Fig. 1. Reactor diagram and sensor arrangement.

Fig. 2. Curves of the concentration change in time for different points of the lower reactor section. $\langle u \rangle = 0.49$ m/h; 1) point 9, 2) 10, 3) 11, 4) 12. C pulse/sec, T, min.

The averaged equation of nonstationary diffusion of a "passive" impurity in a flow with arbitrary velocity profile and initial condition of impulsive insertion of a display is the classical Taylor problem. A flow with uniform velocity profile was considered as the unperturbed problem. As shown in [10], the average diffusion equation is an asymptotic series whose terms are linear combination of the mean concentration $\langle C \rangle$ over the section in the time and axial coordinate while the coefficients depend on the degree of nonuniformity of the velocity profile and the efficiency of the radial mixing in the system. Estimates performed in [10] showed that utilization of a trinomial equation is sufficient for the majority of chemical technology processes but the accuracy of the computation can be raised, if necessary (low H/R ratio, large nonuniformity of the velocity profile) by utilizing subsequent terms of the series. A method of experimental determination of the problem parameters is proposed in [10] — the method of investigating the distribution function of the fluid residence time in the channel. The problem parameters — the factor of velocity profile inhomogeneity A_1 and the radial Peclet number Pe_r, are easily determined by a computation for a known velocity profile. The stationary diffusion problem in a channel with arbitrary velocity profile is examined in this paper in the presence of a source in the form of a homogeneous first order chemical reaction.

Now we write the stationary equation of the change in concentration in a cylindrical channel during progress of a first-order chemical reaction in its volume. We direct the X axis along the channel length and the r axis along its radius, where $r = 0$ on the channel axis. Since the coordinate axes are determined by the conditions of a hydrodynamically stabilized flow in a tube, the matrix $[D]$ should be diagonal. We discard the term responsible for longitudinal diffusion as small compared with the corresponding convective term and we take into account that the concentration derivatives with respect to the angle are zero in connection with the problem symmetry. Taking these assumptions into account, the diffusion equation takes the form

$$u\frac{\partial C}{dX} - \frac{1}{r}\frac{\partial}{dr}\left(rD_r\frac{dC}{dr}\right) - \alpha_p C = 0. \tag{1}$$

We decompose the velocity, concentration, and coefficient of radial diffusion into mean (over the channel section) and fluctuating components

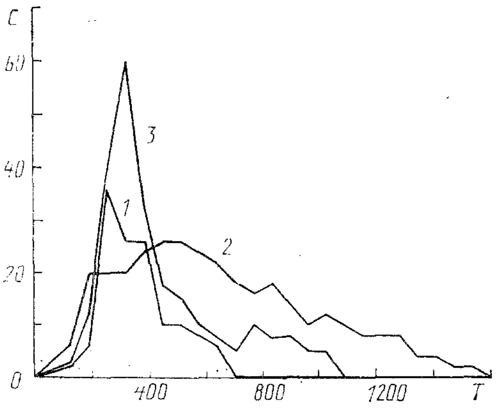

Fig. 3

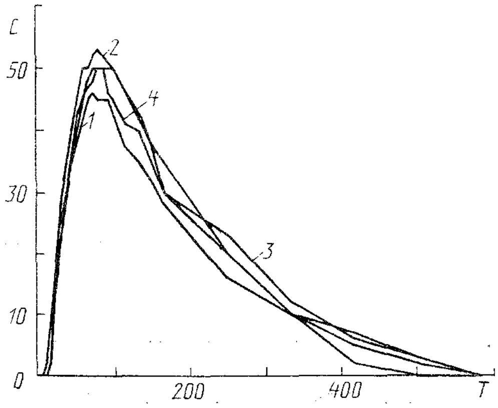

Fig. 4

Fig. 3. Curves of the concentration change in time at points located above each other $\langle u\rangle = 0.49$ m/h: 1) point 1; 2) 5; 3) 9.

Fig. 4. Curves of the concentration change in time for different points of the lower reactor section $\langle u\rangle = 1.63$ m/h. Notation as in Fig. 2.

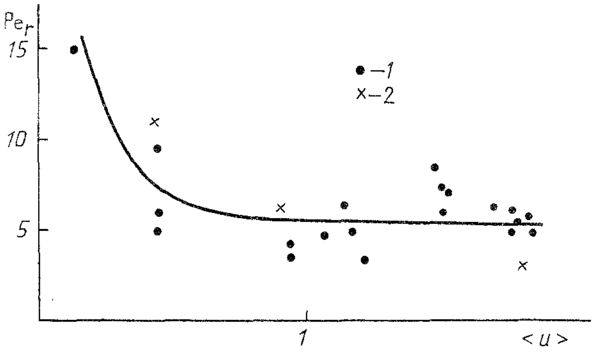

Fig. 5. Dependence of the radial Peclet criterion Pe_r on the reactive mass velocity referred to the total apparatus section: 1) points obtained by a computation on reactor efficiency; 2) points calculated from data of an analysis of the fluid residence time distribution function in the apparatus, $\langle u\rangle$, m/h.

$$u = \langle u\rangle + u'; \quad C = \langle C\rangle + C'; \quad D_r = \langle D_r\rangle + D_r'. \tag{2}$$

Substituting (2) into (1), we find

$$\langle u\rangle \frac{\partial\langle C\rangle}{dX} + \langle u\rangle \frac{dC'}{dX} + u' \frac{d\langle C\rangle}{dX} + \frac{du'C'}{dX} - \frac{\langle D_r\rangle}{r} \frac{\partial}{\partial r}\left(r\frac{dC'}{dr}\right) - \frac{1}{r}\frac{\partial}{\partial r}\left(rD_r' \frac{\partial C'}{\partial r}\right) - \alpha_p\langle C\rangle - \alpha_p C' = 0. \tag{3}$$

Taking the average of (3) over the channel section, we obtain

$$\langle u\rangle \frac{\partial\langle C\rangle}{\partial X} + \frac{\partial\langle u'C'\rangle}{\partial X} - \alpha_p\langle C\rangle = 0. \tag{4}$$

We subtract (4) from (3), by neglecting the term $(1/r)(\partial/\partial r)rD'_r(\partial C'/\partial r)$ which, as shown in [10], does not introduce noticeable error in the calculation

$$\langle u \rangle \frac{\partial C'}{\partial X} + \frac{\partial u'C'}{\partial X} - \frac{\partial \langle u'C' \rangle}{\partial X} - \frac{\langle D_r \rangle}{r} \frac{\partial}{\partial r}\left(r \frac{\partial C'}{\partial r}\right) - \alpha_r C' = -u' \frac{\partial \langle C \rangle}{\partial X}. \tag{5}$$

Taking in dimensionless form

$$Z = \frac{X}{H}; \quad \rho = \frac{r}{R}; \quad \mathrm{Pe}_r = \frac{\langle u \rangle R^2}{\langle D_r \rangle H}; \quad \alpha = \frac{\alpha_r H}{\langle u \rangle}; \quad u' = \frac{u'}{\langle u \rangle}, \tag{6}$$

in place of (4) and (5), we obtain

$$\frac{\partial \langle C \rangle}{\partial Z} - \alpha \langle C \rangle = -\frac{\partial \langle u'C' \rangle}{\partial Z}, \tag{7}$$

$$\frac{\partial C'}{\partial Z} - \frac{1}{\mathrm{Pe}_r} \frac{1}{\rho} \frac{\partial}{\partial \rho}\left(\rho \frac{\partial C'}{\partial \rho}\right) - \alpha C' = -u' \frac{\partial \langle C \rangle}{\partial Z} - u' \frac{\partial C'}{\partial Z} + \frac{\partial \langle u'C' \rangle}{\partial Z}. \tag{8}$$

The boundary conditions for (8) are determined by profile symmetry with respect to the central axis and by absence of a stream near the tube wall

$$\rho = 0 \quad \frac{\partial C'}{\partial \rho} = 0; \quad \rho = 1 \quad \frac{\partial C'}{\partial \rho} = 0. \tag{9}$$

Now we seek the solution of (8) by considering $\partial\langle C\rangle/\partial Z$ a parameter and the terms $u'(\partial C'/\partial Z) + \partial\langle u'C'\rangle/\partial Z$ certain small corrections. Thus, we write the Green's function for (8)

$$G(Z, Z_0, \rho, \rho_0) = \frac{2}{\mathrm{Pe}_r} \sum_{i=1}^{\infty} E_i \frac{j_0(\lambda_i \rho)\, j_0(\lambda_i \rho_0)}{j_0^2(\lambda_i)}, \tag{10}$$

where, because of (9), the eigenvalues λ_i are roots of the equation

$$j_1(\lambda_i) = 0, \quad E_i = \exp\left[-\left(\frac{\lambda_i^2}{\mathrm{Pe}_r} - \alpha\right)(Z - Z_0)\right].$$

We take as the initial condition

$$Z = 0 \quad C' = 0. \tag{11}$$

Substituting (10) into the equation for C' and taking account of (11) we obtain

$$C' = -\int_0^Z \int_0^1 \sum_{i=1}^{\infty} \frac{2}{j_0(\lambda_i)^2} E_i j_0(\lambda_i \rho)\, j_0(\lambda_i \rho_0)\, \rho_0 \times \left[u'(\rho_0) \frac{\partial \langle C \rangle}{\partial Z_0} + u'(\rho_0) \frac{\partial C'}{\partial Z_0} - \frac{\partial \langle u'C' \rangle}{\partial Z_0}\right] dZ_0 d\rho_0. \tag{12}$$

We use an iteration method to solve the integrodifferential equation (12), in conformity with which we assume $C' = C_n'$ under the integral in evaluating C_{n+1}'. We take $C_0' = 0$ for the initial approximation. We write the equation for C_1':

$$C_1' = -\int_0^Z \int_0^1 \sum_{i=1}^{\infty} \frac{2}{j_0^2(\lambda_i)} E_i j_0(\lambda_i \rho)\, j_0(\lambda_i \rho_0)\, \rho_0 u'(\rho_0) \frac{\partial \langle C \rangle}{\partial Z_0} dZ_0 d\rho_0. \tag{13}$$

As shown in [10], integration with respect to ρ_0 can be performed on (13) for each specific velocity profile, but it is impossible to integrate with respect to Z_0 since $\langle C\rangle$ is an unknown function of Z. Consequently, integrating (13) with respect to ρ_0, multiplying C' by u', and taking the average of the product obtained over the section of the apparatus, we obtain

$$\langle u'C' \rangle = -\int_0^Z \sum_{i=1}^{\infty} K_i E_i \frac{\partial \langle C \rangle}{\partial Z_0} dZ_0, \tag{14}$$

where K_i are certain constants determined by the velocity profile and identical to the appropriate constants in [10].

We substitute (14) into (7)

$$\frac{d\langle C \rangle}{dZ} - \alpha \langle C \rangle = \frac{d}{dZ} \int_0^Z \sum_{i=1}^{\infty} K_i E_i \frac{d\langle C \rangle}{dZ_0} dZ_0. \tag{15}$$

We introduce the new variable

$$C^* = \langle C \rangle \exp(-\alpha Z). \tag{16}$$

Substituting (16) into (15), we find

$$\begin{gathered}\frac{dC^*}{\partial Z} - \frac{d}{dZ} \int_0^Z \sum_{i=1}^{\infty} K_i E_{1i} \left(\frac{dC^*}{dZ_0} + \alpha C^* \right) dZ_0 = \sum_{i=1}^{\infty} K_i \left(\frac{dC^*}{dZ} + \alpha C^* \right) - \\ - \int_0^Z \sum_{i=1}^{\infty} K_i E_{1i} \frac{\lambda_i^2}{\mathrm{Pe}_r} \left(\frac{dC^*}{dZ_0} + \alpha C^* \right) dZ_0; \quad E_{1i} = \exp\left[-\frac{\lambda_i^2}{\mathrm{Pe}_r} (Z - Z_0) \right].\end{gathered} \tag{17}$$

Next we differentiate (17) with respect to Z, multiply by $\mathrm{Pe}_r/\lambda_1^2$, and add the expression obtained to (17) to obtain

$$\begin{gathered}\frac{dC^*}{dZ} + \frac{\mathrm{Pe}_r}{\lambda_1^2} \frac{d^2C^*}{dZ^2} = \sum_{i=1}^{\infty} K_i \left(\frac{d^2C^*}{dZ^2} + \alpha \frac{dC^*}{dZ} \right) - \sum_{i=2}^{\infty} K_i \left(\frac{\lambda_i^2}{\lambda_1^2} - 1 \right) \left(\frac{dC^*}{dZ} + \alpha C^* \right) + \\ + \int_0^Z \sum_{i=2}^{\infty} K_i \frac{\lambda_i^2}{\mathrm{Pe}_r} \left(1 - \frac{\lambda_i^2}{\lambda_1^2} \right) E_{1i} \left(\frac{dC^*}{dZ_0} + \alpha C^* \right) dZ_0.\end{gathered} \tag{18}$$

Differentiating (18) with respect to Z, multiplying by $\mathrm{Pe}_r/\lambda_2^2$, and adding the expression obtained to (18), we eliminate the integral with $\exp[-\lambda_2^2(Z - Z_0)/\mathrm{Pe}_r]$. Continuing this procedure further theoretically to infinity, and substituting the value of C^* and its derivatives into the final expression, we find that the averaged diffusion equation with a first-order chemical reaction has the form

$$\begin{gathered}-\alpha \langle C \rangle \left[1 - \sum_{i=1}^{\infty} \frac{\alpha \mathrm{Pe}_r}{\lambda_i^2} + \sum_{\substack{i=1 \\ j=i+1}}^{\infty} \frac{\alpha^2 \mathrm{Pe}_r^2}{\lambda_i^2 \lambda_j^2} - \sum_{\substack{i=1 \\ j=i+1 \\ k=j+1}}^{\infty} \frac{\alpha^3 \mathrm{Pe}_r^3}{\lambda_i^2 \lambda_j^2 \lambda_k^2} + \ldots \right] + \\ + \frac{d\langle C \rangle}{dZ} \left[1 - \sum_{i=1}^{\infty} \frac{2\alpha \mathrm{Pe}_r}{\lambda_i^2} + \sum_{\substack{i=1 \\ j=i+1}}^{\infty} \frac{3\alpha^2 \mathrm{Pe}_r^2}{\lambda_i^2 \lambda_j^2} - \sum_{\substack{i=1 \\ j=i+1 \\ k=j+1}}^{\infty} \frac{4\alpha^3 \mathrm{Pe}_r^3}{\lambda_i^2 \lambda_j^2 \lambda_k^2} + \ldots \right] + \\ + \frac{1}{\alpha} \frac{d^2\langle C \rangle}{dZ^2} \left[\sum_{i=1}^{\infty} \frac{\alpha \mathrm{Pe}_r}{\lambda_i^2} - \sum_{\substack{i=1 \\ j=i+1}}^{\infty} \frac{3\alpha^2 \mathrm{Pe}_r^2}{\lambda_i^2 \lambda_j^2} + \sum_{\substack{i=1 \\ j=i+1 \\ k=j+1}}^{\infty} \frac{6\alpha^3 \mathrm{Pe}_r^3}{\lambda_i^2 \lambda_j^2 \lambda_k^2} - \ldots \right] + \\ + \frac{1}{\alpha^2} \frac{d^3\langle C \rangle}{dZ^3} \left[\sum_{\substack{i=1 \\ j=i+1}}^{\infty} \frac{\alpha^2 \mathrm{Pe}_r^2}{\lambda_i^2 \lambda_j^2} - \sum_{\substack{i=1 \\ j=i+1 \\ k=j+1}}^{\infty} \frac{4\alpha^3 \mathrm{Pe}_r^3}{\lambda_i^2 \lambda_j^2 \lambda_k^2} + \right. \\ \left. + \sum_{\substack{i=1 \\ j=i+1 \\ k=j+1 \\ l=k+1}}^{\infty} \frac{10\alpha^4 \mathrm{Pe}_r^4}{\lambda_i^2 \lambda_j^2 \lambda_k^2} - \ldots \right] + \ldots = -\alpha \mathrm{Pe}_r \sum_{m=1}^{\infty} \frac{K_m}{\lambda_m^2} \frac{d\langle C \rangle}{dZ} \left[1 - \sum_{i=1}^{\infty} \frac{\alpha \mathrm{Pe}_r}{\lambda_i^2} + \sum_{\substack{i=1 \\ j=i+1}}^{\infty} \frac{\alpha^2 \mathrm{Pe}_r^2}{\lambda_i^2 \lambda_j^2} - \ldots \right] + \\ + \mathrm{Pe}_r \frac{d^2\langle C \rangle}{dZ^2} \sum_{m=1}^{\infty} \frac{K_m}{\lambda_m^2} \left[1 - \sum_{i=1}^{\infty} \frac{2\alpha \mathrm{Pe}_r}{\lambda_i^2} + \sum_{\substack{i=1 \\ j=i+1}}^{\infty} \frac{3\alpha^2 \mathrm{Pe}_r^2}{\lambda_i^2 \lambda_j^2} - \ldots \right] +\end{gathered}$$

$$+\frac{\mathrm{Pe}_r}{\alpha}\frac{d^3\langle C\rangle}{dZ^3}\sum_{m=1}^{\infty}\frac{K_m}{\lambda_m^2}\left[\sum_{i=1}^{\infty}\frac{\alpha\mathrm{Pe}_r}{\lambda_i^2}-\sum_{\substack{i=1\\ j=i+1}}^{\infty}\frac{3\alpha^2\mathrm{Pe}_r^2}{\lambda_i^2\lambda_j^2}+\right.$$

$$\left.+\sum_{\substack{i=1\\ j=i+1\\ k=j+1}}^{\infty}\frac{6\alpha^3\mathrm{Pe}_r^3}{\lambda_i^2\lambda_j^2\lambda_k^2}-\ldots\right]+\frac{\mathrm{Pe}_r}{\alpha^2}\frac{d^4\langle C\rangle}{dZ^4}\sum_{m=1}^{\infty}\frac{K_m}{\lambda_m^2}\left[\sum_{\substack{i=1\\ j=i+1}}^{\infty}\frac{\alpha^2\mathrm{Pe}_r^2}{\lambda_i^2\lambda_j^2}-\right.$$

$$\left.-\sum_{\substack{i=1\\ j=i+1\\ k=j+1}}\frac{4\alpha^3\mathrm{Pe}_r^3}{\lambda_i^2\lambda_j^2\lambda_k^2}+\sum_{\substack{i=1\\ j=i+1\\ k=j+1\\ l=k+1}}\frac{10\alpha^4\mathrm{Pe}_r^4}{\lambda_i^2\lambda_j^2\lambda_k^2\lambda_l^2}-\ldots\right]+\ldots$$

$$m\neq i\neq j\neq k\neq l. \tag{19}$$

Equation (19) is quite interesting in many respects. First, there follows from it that upon taking the average of local parabolic transport equations for an active impurity, a differential equation can be obtained that is an infinite asymptotic series in the derivative of the mean concentration over the apparatus section with coefficients that depend on the degree of transverse nonuniformity in the system, the chemical reaction rate, and the radial substance transport velocity (Pe_r), which was given a theoretical foundation in [11, 12]. Second, as follows from (19), upon taking the average of two-dimensional transport equations, additional convective and source-like terms appear, i.e., effects occur that are analogous to the phenomenon of directional transport in inhomogeneous turbulence [13] and the dynamo effect in magnetohydrodynamics [14], as was mentioned earlier [15]. As follows from (19), the coefficient of the second derivative $d^2\langle C\rangle/dZ^2$ is positive. However, the concept of a "dispersion flow" has a much wider sense in this case since it includes the term $\langle u'C'\rangle = \sum\limits_{i=2}^{\infty} F_i d^i\langle C\rangle/dZ_i$ exactly as the total concentration gradient equals $d/dZ[\sum\limits_{i=0}^{\infty} F_i d^i\langle C\rangle/dZ_i]$ and because of the sign-variability of the series (19) the total dispersions flow is directed to the side opposite to the direction of the total concentration gradient.

For very large values of the channel length Z the derivative $d\langle C\rangle/dZ_0$ ceases to depend on Z_0, Eq. (13) can be integrated with respect to Z_0, and the term $d\langle u'C'\rangle/dZ$ in (7) takes the form

$$-\frac{d\langle u'C'\rangle}{dZ}=\sum_{i=1}^{\infty}K_i\frac{\mathrm{Pe}_r}{\lambda_i^2}\frac{d^2\langle C\rangle}{dZ^2}. \tag{20}$$

Substituting (20) into (7), we obtain the usual diffusion equation

$$\frac{d\langle C\rangle}{dZ}-\alpha\langle C\rangle=\frac{1}{\mathrm{Pe}_e}\frac{d^2\langle C\rangle}{dZ^2}$$

with effective diffusion coefficient $1/\mathrm{Pe}_e$ equal to $\mathrm{Pe}_r\sum\limits_{i=1}^{\infty} K_i/\lambda_i^2$. The remaining terms in the series (19) equal zero in this case. It is important to note that the criteria Pe_r and $A_1=\sum\limits_{i=1}^{\infty} K_i/\lambda_1^2$ agree completely with the corresponding criteria obtained when taking the average of the nonstationary transport equation for a passive impurity in [10], which affords a possibility for using the data obtained in investigating the residence time distribution function on cold test-stands for reactor analysis. As is shown in [10], the effective diffusion coefficient equals the Taylor dispersion coefficient exactly. In the absence of a reaction ($\alpha = 0$), Eq. (19) goes over into the stationary analog of (1.15) in [10].

The well-founded estimate of the quantities needed to compute the terms of the series (19) is of great practical interest. As is shown in [10], the radical Peclet criterion Pe_r is within the limits of approximately 5 to 10 in different kinds of chemical apparatus. The dimensionless chemical reaction rate constant α is of the order 10^{-2}-10^{-1}, $H/R \sim 4$-6 for the majority of reactions. Consequently, even under careful estimates the product $\mathrm{Pe}_r\alpha$ is of the order 0.1-1.0. We estimate the contribution of different terms of the series (14) to (19) with this condition. Let $Z = 1$ (yield from the reactor). The Z_0 found by the theorem of the mean equals 0.5645 for the first term, 0.677 for the second, and 0.775 for the third. Without taking account of the differences in the coefficients K_i, the second term of the equation here is approximately 10% of the first, and the third is ~5%. If we take into account that the coefficients K_i for a turbulent flow differ by a factor of five (by one order for laminar flow) and $K_2 = 0.24\,K_1$, $K_3 = 0.24\,K_1$ even in the case of the greatest transverse nonuniformity investigated in [10], then it is clear that for $\alpha \sim 0.1$ it is sufficient to take just the first term of the series in the computation. For $\alpha \sim 1$ estimates made in [10] will be legitimate and a trinomial equation

$$F_1 \frac{d\langle C\rangle}{dZ} + F_2 \frac{d^2\langle C\rangle}{dZ^2} + F_3 \frac{d^3\langle C\rangle}{dZ^3} - \alpha\langle C\rangle = 0, \tag{21}$$

should be recommended for practical computations, where

$$\begin{aligned} F_1 &= F_{11}[1 + A_1\alpha\,\mathrm{Pe}_r(0{,}957 - 0{,}024\alpha\,\mathrm{Pe}_r)];\\ F_2 &= F_{12}[1 - A_1\,\mathrm{Pe}_r F_{11}(0{,}917 - 0{,}0268\alpha\,\mathrm{Pe}_r)];\\ F_3 &= F_{13}[1 - A_1\,\mathrm{Pe}_r F_{12}(0{,}468 - 0{,}00958\alpha\,\mathrm{Pe}_r)]; \end{aligned} \tag{22}$$

F_{11}, F_{12}, F_{13} are constants formed by dividing the coefficients of the different terms in the left side in (19) by the coefficient of the term $\alpha\langle C\rangle$; $A_1 = \sum_{i=1}^{\infty} K_i/\lambda_i^2$ is the inhomogeneity parameter of the velocity profile, which is identical to the corresponding parameter in [10]. The factors in the square brackets in (22) approximate the corresponding terms in (19) with a 7-8% rms error.

We find the boundary conditions to (21) as follows. Let a uniform flow (in concentration) with the relative concentration

$$\langle C\rangle = \frac{C}{C_0} = 1. \tag{23}$$

come in to the apparatus entrance. Substituting (23) into (15) and passing to the limit as $Z \to 0$ we find

$$\frac{d\langle C\rangle}{dZ} = \alpha\langle C\rangle. \tag{24}$$

Thus, we obtain

$$\frac{d^2\langle C\rangle}{dZ^2} = \alpha\frac{d\langle C\rangle}{dZ} = \alpha^2\langle C\rangle. \tag{25}$$

As our computations show, the coefficient of the highest derivative $d^3\langle C\rangle/dZ^3$ is relatively small; therefore, the solution of (21) can be sought by the method of an expansion in series of a small parameter. The constants in (22) — the transverse nonuniformity criterion of the velocity field A_1 and the radial Peclet criterion — can, as already noted, be found by methods for investigating the residence time distribution function of the fluid in the apparatus, and the chemical reaction rate constant α can be found from ordinary kinetic experiments.

The theory was confirmed experimentally on a 3400-mm-diameter operating chemical reactor for the synthesis of diphenylol propane from phenol and acetone using an ion-exchange resin KU-2-8 "c.p." as catalyst, which was in the fluidized state under the working conditions of reactor operation. The fluid flow configuration was investigated by the method of radioactive indicators where orthonitrobromobenzene, tagged Br-82, well dissolved in phenol and acetone were used as tracers. The isotope is a γ-emitter, which permitted recording it through the apparatus wall. The isotope half-life period is 36 h, which is sufficient for reliability of the experiment results. The tests were performed by the pulse method, where the pulse (radiometer MVR-5) was recorded at the reactor entrance and exit and 12 points thereon along its height (four in each section). The diagram of the sensor arrangement is shown in Fig. 1. Typical curves of the changes in concentration in time in one reactor section (Figs. 2 and 4) and at points located directly above each other at different modes of its operation (Fig. 3) are presented in Figs. 2-4.

As follows from Fig. 2, for small reaction mass velocities in the apparatus the time of indicator incidence at the most remote point from the distributive lattice is often less than the time of its incidence on close-lying sections. Such a pattern of the concentration distribution is possible in the presence of bypass flows and complex circulation systems in the reactor. As the reaction mass velocity increases the concentration profiles equilibrate, and as is seen from Fig. 4, the concentration measured in one section are nearly in agreement.

The flow configuration in the apparatus was estimated by the concentration curve recorded at the emergence of the reaction mass from the apparatus, for whose analysis the expressions derived in [10] were used. Attempts to process the test data by the ordinary Taylor diffusion equation or by the telegraph equation (1.17) in [10] proved unsuccessful since the moment of the fluid residence time distribution function I differed significantly from unity in practically all the tests, which can be explained, as is shown in [10], just within the framework of the present model. The search for the parameters was performed by minimizing the functional

$$F = \int\limits_{0,01}^{10} [\tilde{C}_{\text{opt}} - \tilde{C}_{\text{calc}}]^2 \, dS,$$

where S is the Laplace variable.

As follows from Fig. 5, in which test points of the measurement data 2 are superposed (each point is the mean value of 6-13 tests), the radial Peclet criterion decreases from 12 to 2 as the fluid velocity increases.

In order to obtain data about the reactor efficiency, multiple examinations were performed in different modes of its operation. Although the kinetics of this process are quite complex, it can be computed according to the model developed in this paper since the reaction is performed in practice in a large excess of phenol (a phenol/acetone ratio of 10), and consequently, it can be taken that the reaction is of first order in acetone with a sufficient degree of accuracy.

Since the radial Peclet number was of the order of 2-5 in the majority of reactor operating modes according to measurement data on a cold test-stand, while the dimensionless chemical reaction rate constant α equals 1-2 for this system, the product $\alpha \mathrm{Pe}_r$ should be within the limits 5-10 and the applicability of the trinomial equation (21) should additionally be given as foundation. The results of computing the coefficients F_2/F_1, F_3/F_1, and F_4/F_1 for $\alpha \mathrm{Pe}_r = 5$ and 10 are presented below for different values of the velocity field inhomogeneity coefficient (%)

	$\alpha \mathrm{Pe}_r = 5$			$\alpha \mathrm{Pe}_r = 10$		
$A_1 \cdot 10^{-4}$	F_2/F_1	F_3/F_1	F_4/F_1	F_2/F_1	F_3/F_1	F_4/F_1
6,275	39,04	6,27	0,53	30,77	4,36	0,35
7,502	39,04	6,27	0,53	30,75	4,35	0,35
9,172	38,98	6,26	0,52	30,72	4,35	0,35
11,524	38,92	6,24	0,52	30,69	4,34	0,35
12,233	38,90	6,23	0,52	30,66	4,33	0,35
13,101	38,89	6,23	0,52	30,66	4,33	0,35
69,161	37,55	5,85	0,48	29,76	4,09	0,32
177,264	34,87	5,09	0,40	27,89	3,61	0,28
208,332	34,45	4,88	0,39	27,76	3,66	0,28
362,262	30,34	3,72	0,24	24,34	2,70	0,175

As is seen, for all values of the degree of transverse nonuniformity of the velocity profile, the coefficient of the third terms of the series exceeds by more than an order the coefficient of the fourth term. Estimates show that for small degrees of transverse nonuniformity of the velocity profile ($A_1 = 6 \cdot 10^{-4}$) $|d^4\langle C\rangle/dZ^4|_{Z=1} \approx |d^3\langle C\rangle/dZ^3|_{Z=1}$ and for a high degree of transverse nonuniformity ($A_1 = 2 \cdot 10^{-2}$) $|d^4\langle C\rangle/dZ^4|_{Z=1} \approx 1.3|d^3\langle C\rangle/dZ^4|_{Z=1}$; therefore, utilization of the trinomial (21) is completely adequate for processing the test results.

In connection with the fact that the reaction rate constant and the physical properties of the mixture vary noticeably over the apparatus height, the measurement results were processed as follows. For each reactor operating mode, the system of equations

$$F_1 \frac{d\langle C_j\rangle}{dZ} + F_2 \frac{d^2\langle C_j\rangle}{dZ^2} + F_3 \frac{d^3\langle C_j\rangle}{dZ^3} + f_1(\langle C_j\rangle, \langle T\rangle) = 0, \tag{26}$$

$$F_1 \frac{d\langle T\rangle}{dZ} + F_2 \frac{d^2\langle T\rangle}{dZ^2} + F_3 \frac{d^3\langle T\rangle}{dZ^3} + f_2(\langle C_j\rangle, \langle T\rangle) = 0 \tag{27}$$

was solved jointly on an electronic computer with the boundary conditions (24) and (25). The subscript j in (26) and (27) refers to different components of the reactive mixture, while f_1 and f_2 are equations of the kinetics of the diphenylolpropane synthesis reaction.

The computational method terminates in the selection of the model parameters (A_1 and Pe_r) that satisfy the experimental curve of the concentration and temperature changes along the reactor height. For a numerical solution of the problem, the system (26) and (27) goes over into a system of ordinary first-order differential equations by the usual substitution

$$\langle C_{1j}\rangle = \frac{d\langle C_j\rangle}{dZ}; \quad \langle C_{2j}\rangle = \frac{d\langle C_{1j}\rangle}{dZ}$$

solved using linear multistep Adams and Gear methods [26].

Results of computing the radial Peclet number found from data on reactor efficiency are presented in Fig. 5. Superposed there are points obtained by investigating the fluid residence time distribution function. As follows from the figure, the values of the criterion Pe_r found by the different methods are in satisfactory agreement.

Analysis of Fig. 5 shows that as the fluid velocity increases Pe_r diminishes, and starting with approximately the velocity $3 \cdot 10^{-4}$ m/sec becomes equal to 5. It is characteristic that this velocity corresponds to the velocity of the beginning of fluidization for this system, to which large homogeneity of the fluidization model is inherent because of the extremely close values of the ionite and reactive mass densities. For low fluid velocities, the layer "sat" partially, i.e., was mainly in a fixed state, where irregular ejections of fluid were observed at separate sites of the layer, which was due to the large transverse nonuniformity of the velocity and concentration profiles. It is interesting to note that the value $\mathrm{Pe}_r = 5$ found in tests agrees with the estimates made above. The dependence of the criterion A_1 on the fluid velocity is analogous in nature to the dependence presented in Fig. 5. For low fluid velocities A_1 is of the order of 0.01-0.015, then drops to the value 0.001-0.002. The uniform fluidization mode that holds in the majority of reactor operating modes, the absence of circulation currents predetermined the success of utilizing the theory developed in this paper since all the equations of the model are obtained under the assumption of constancy of the velocity profile along the apparatus height. For low reactive mass velocities, when the fluidization mode was known to be inhomogeneous, the computation can only be considered approximate.

CONCLUSIONS

1. A stationary diffusion differential equation is derived by the "perturbation" method for the mean concentration over the channel for an inhomogeneous velocity profile and the presence of sources in the form of a first-order chemical reaction. It is shown that the differential equation is an asymptotic series in the derivative of the mean concentration over the channel section with coefficients dependent on the degree of transverse nonuniformity of the velocity profile, the efficiency of the radial mixing in the system, and the chemical reaction rate constants. Additional convective and source-like terms are a characteristic feature of the averaged equation.

2. Estimates are carried out showing that terms with derivatives to the third order must be taken into account to achieve the required computation accuracy up to values of $\alpha\mathrm{Pe}_r \sim 10$. Under conditions of a small ratio between the channel length and radius or a high chemical reaction rate, the accuracy of the computation can be raised by using higher-order terms.

3. It is shown that the unknown parameters of the problem: the criterion of the velocity profile inhomogeneity and the radial Peclet criterion can be found in an independent experiment investigating the fluid residence time distribution function.

4. The equations obtained in the paper are more general than those in the literature. The Taylor model and the hyperbolic equations being discussed in the literature at this time enter as a particular case therein.

5. It is shown that the system "memory" is not constrained by the introduction of an additional term

$d^2\langle C\rangle/d\tau^2$ (in a system moving with the mean flow velocity) but includes derivatives of all orders. Utilization of some number of terms of the series should be due to specific conditions of the problem under consideration.

6. The theory is confirmed experimentally according to data of operation of an industrial reactor for synthesis of diphenylolpropane of 3.4-m diameter with a fluidized bed of ionites as catalyst. Satisfactory agreement is obtained between parameters of the problem found in an experiment investigating the fluid residence time distribution function in the apparatus and data investigating its operating efficiency.

NOTATION

Here C is the concentration; D, diffusion coefficient; H, reactor height; r, running radius; R, apparatus radius; u, velocity; X, longitudinal coordinate; α_p, reaction rate constant. The criteria are: $\mathrm{Pe}_r = (\langle u\rangle R^2)/(\langle D_r\rangle H)$ is the radial Peclet criterion, $A_1 = \sum_{i=1}^{\infty} K_i/\lambda_i^2$ is the velocity field inhomogeneity parameter in the apparatus; $\mathrm{Pe}_e = (\mathrm{Pe}_r A_1)^{-1}$ is the effective Peclet criterion. The angular brackets denote taking the average over the area of the apparatus; the "prime" sign ′ refers to fluctuating quantities (over the section). Subscripts: r is the radial and e is for effective.

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