MASS TRANSFER IN HETEROGENEOUS CHEMICAL REACTORS UNDER VARIABLE HYDRODYNAMIC CONDITIONS

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The equation of convective diffusion is solved for a channel with a longitudinal variation of velocity and a laminar flow. A formula is derived for the thickness of the diffusion boundary layer.

In the design of various chemical engineering processes there arises the problem of optimizing the mass transfer in reactors of the liquid—solid type, where the solid phase consists of monolithic plates wetted by the liquid. In addition to chemical reactors where various solid substances are dissolved, such designs are found in the electrochemical industry (electrolyzers, electrochemical current generators with expendable anodes [1]) and in special-purpose workshops.

A system of this kind is shown schematically in Fig. 1. Pump 1 feeds a liquid solution of reactants from container 4 to reactor 2, where a reaction between liquid and solid ingredients takes place. The products of this reaction are then removed from the circulating liquid and out of the system. The resupply of reactants and the exhaust of products may be effected continuously or periodically at the appropriate location in the system as, for example, in container 1. * The number of circulation cycles may also be varied.

We will consider here only the one-phase flow of a liquid with dissolved reactants and products, where hydrodynamic processes usually play a very important role. Generally, the rate of the technological process in a reactor is determined by the "hybrid" kinetics; within the initial segment of an active channel the process is limited by chemical reactions, but, as a diffusion boundary layer builds up in the subsequent channel segments, the mass transfer processes become limiting. The problem of determining the process parameters of hybrid kinetics has been discussed in many original studies and in surveys, among which reference will be made to monographs [3] and [4] with listed bibliographies.

It has been shown in [4] that a solution of the problem based on assuming a uniformly accessible surface ensures a practically acceptable accuracy, with an error at most 5% larger than the error of more complicated methods. With the aid of the formulas given in [3], it is possible to determine the thickness of the diffusion boundary layer and other local or mean values of mass transfer parameters.

For laminar flow in medium-length channels, where $\delta_d \ll R$ may be assumed, we have

$$\delta_d = \frac{1}{0.69}\left(\frac{D}{\nu}\right)^{1/3}\sqrt[3]{\frac{\nu}{uR}}\sqrt[3]{R^2x}. \quad (1)$$

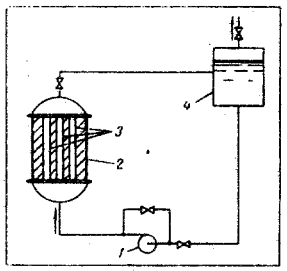

Fig. 1. Schematic diagram of the system.

In viscous liquids δ_d is approximately equal to $\delta_b/10$, the latter thickness being based on $u_b = 0.99u_\infty$.

For turbulent flow we have

$$\delta_d \approx \frac{a\delta\nu}{\mathrm{Pr}^{1/4}} \approx \frac{1}{5}\frac{a\nu}{u^*}. \quad (2)$$

*Various modifications of this system for resupplying the reactant solution have been analyzed in several other studies (in [2], for instance).

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In this flow mode $\delta_d \approx d_v/5$, with δ_d varying only slightly along the channel, and $u^x = \sqrt{\tau/\rho}$.

The practical application of these formulas requires that they be refined in several ways:

the velocity of the liquid can vary appreciably along the channel;

the flow mode (laminar, turbulent, or transitional) can also change from segment to segment along the channel;

the solid surfaces 3 (Fig. 1) in the stream are characterized by a definite roughness and this may substantially affect the hydrodynamics.

A variation in velocity may be due to the variable channel section and also due to more complex causes (the existence of hydrodynamically different channel segments: flooding of the jet, reversal and circulation zones, etc.). In an attempt to calculate the diffusion layer under these conditions, one may approximate the velocity profile along the axis of abscissas and then solve the problem analytically. A power-law profile $u = Ku_0x^m$ is often used in hydromechanics for simplifying the boundary-layer equations in the exterior problem. Moreover, the equations may be reduced to dimensionless form, or an appropriate dimension and numerical value may be selected for the constant K (K = 1, for instance). The value of exponent m depends on the trend of the velocity variation: in an accelerated stream $m > 0$, in a decelerated stream $m < 0$. It must be remembered here that the boundary layer separates, formally, when $m \leq -0.09$ and the solution becomes meaningless [5] then. In practice, however, separation may depend on other factors as well, and in every individual case one must ascertain the actual flow mode on the basis of all factors affecting it.

Assuming a power-law relation $u = u_0x^m$ and considering that, according to [3], $u \approx u_0 2y/\mathrm{Re}$ (for medium-length channels), we obtain the equation of convective diffusion in a channel with variable velocity and laminar flow:

$$\frac{2u_0}{R_e} yx^m \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial y^2}. \tag{3}$$

This equation differs from that in [3] by including the factor x^m, and it can be solved by inserting the dimensionless quantity η:

$$\eta = \left[\frac{u_0(1-m)}{DR_a}\right]^{1/3} x^{\frac{m-1}{3}} y. \tag{4}$$

Then Eq. (3) transforms into

$$\frac{d^2c}{d\eta^2} + \frac{2}{3}\frac{dc}{d\eta} = 0, \tag{5}$$

the solution to which is well known.

The boundary conditions are

$$\begin{gathered} c = c_0 \quad \text{for} \quad y = R, \quad x = 0, \\ c = 0 \quad \text{for} \quad y = 0. \end{gathered} \tag{6}$$

The solution to Eq. (5) which satisfies the boundary conditions (6) is

$$c = \frac{c_0 \int_0^z \exp\left(-\frac{2}{9}\eta^3\right) d\eta}{\int_0^\infty \exp\left(-\frac{2}{9}\eta^3\right) d\eta}, \tag{7}$$

$$z = \left[\frac{u_0(1-m)}{DR_e}\right]^{1/3} x^{\frac{m-1}{3}} y.$$

The integral in the denominator can be represented in terms of the gamma function:

$$\int_0^\infty \exp\left(-\frac{2}{9}\eta^3\right) d\eta = \left(\frac{9}{2}\right)^{1/3} \frac{1}{3} \Gamma\left(\frac{1}{3}\right) = 1.45.$$

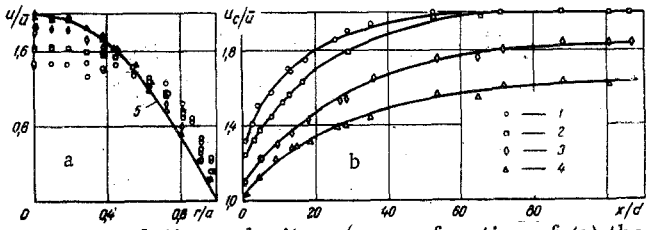

Fig. 2. Relative velocity u/u as a function of (a) the relative channel radius r/*a* at Re = 1200 and (b) the relative channel length x/d at Re = 600-2400; for (a) r/*a*: 1) 8; 2) 17; 3) 35; 4) 71; 5) Eq. (1) for (b) Re: 1) 600; 2) 1200; 3) 1800; 4) 2400.

The expression for the density of the peak diffusion current into the channel wall (at a zero reactant concentration c_s at the surface) is

$$j_d = D\left(\frac{\partial c}{\partial y}\right)_{y=0} = \frac{Dc_0[u_0(1-m)]^{1/3}x^{\frac{m-1}{3}}}{(DR_e)^{1/3}\int_0^\infty \exp\left(-\frac{2}{9}\eta^3\right)d\eta} = 0.69c_0D\left[\frac{u_0(1-m)}{DR_e}\right]^{1/3}x^{\frac{m-1}{3}} = \frac{Dc_0}{\delta_d},$$

from where

$$\delta_d = \frac{(DR_e)^{1/3}x^{\frac{1-m}{3}}}{0{,}69[u_0(1-m)]^{1/3}}. \qquad (8)$$

At m = 0 these have the same form as those given in [3]:

$$j_d = 0.69Dc_0\left(\frac{u}{DR_e x}\right)^{1/3}, \text{ and } \delta_d = \frac{1}{0.69}\left(DR_e\frac{x}{u}\right)^{1/3}.$$

When it is not possible to represent the velocity profile with a single constant exponent m, then the channel may be subdivided into several sufficiently short segments with different exponents m_i. In this case, when δ_d is to be calculated according to formula (8), a fictitious abscissa x_i^f needs to be assigned to the junction point between segments x_{i-1}-x_i and x_i-x_{i+1}, to denote the distance from the initial point of the boundary layer forming while the mean mainstream velocity within segment x_i-x_{i+1} changes with the corresponding exponent $m_{(i-i+1)}$. This abscissa can be defined on the basis of the condition δ_d = idem at the junction point between both segments, namely

$$x_i^f = (0.69\delta_d)^{\frac{3}{1-m_i}}\left[\frac{u_{0i}(1-m_i)}{DR_e}\right]^{\frac{1}{1-m_i}}, \qquad (9)$$

which had been derived from Eq. (8) by raising all its factors to the power $3/(1-m_i)$.

A comparison between the results of calculations according to formulas (9) and (20.10) in [3] respectively indicates that the difference between them is determined by the sign and the magnitude of exponent m. In decelerated streams m < 0 and the value of δ_d according to (8) is higher than according to (20.10) in [3], and conversely. We must note that the formal requirement for the separation of the boundary layer [5] is satisfied at the channel surface in decelerated streams with m ≤ −0.09, which restricts the applicability of the proposed relations.

It is also necessary to refine the definition of the flow mode in the reactor. If the condition Re < Re_{cr} is formally satisfied throughout the channel, this does not mean that no turbulence occurs in the initial segments where the solution enters from an injector or from a circulation tube with, as a rule, developed turbulence.

Unlike the buildup of turbulence, the decay of turbulence in a channel proceeds gradually rather than stepwise along the channel. The test results shown in Figs. 2 and 3, pertaining to transition from turbulent to laminar flow in a channel with two consecutive segments having different diameters each (d_1 = 0.49 cm and d_2 = 2.2 cm), illustrate this [6]. The graphs indicate that, depending on the value of the Reynolds number Re, it takes a channel segment of a relative length x/d ≥ 20 before turbulence vanishes.

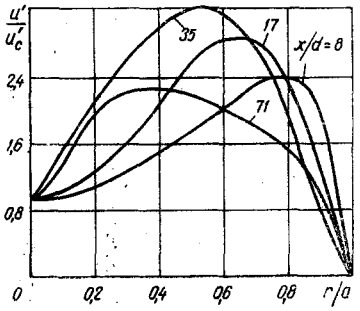

Fig. 3. Velocity profile in channels of various relative lengths x/d.

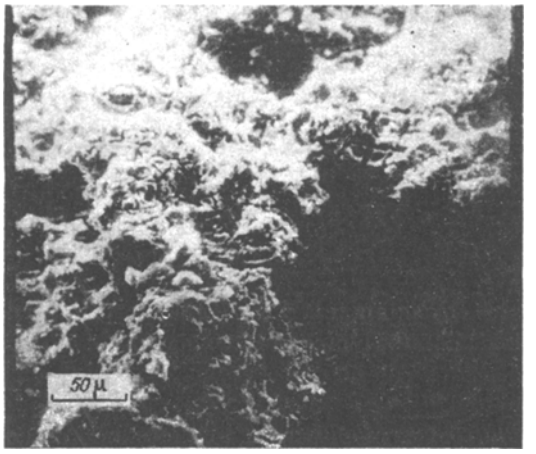

Fig. 4. Surface of an expended metal plate.

Furthermore, an evaluation of the flow mode in a channel must take into account the shape and the finish of the solid surface. The relations derived here apply to hydrodynamically smooth surfaces, and this is by far not always the case. The photograph in Fig. 4 shows an expended metal plate in one of such reactors, taken under an electron-raster microscope and indicating a high degree of overall roughness (up to $h_r = 0.3$ mm). With asperities as high as this, turbulence may start already when $u^x \approx 0.2$ cm/sec, inasmuch as at such a velocity and with $\nu = 10^{-2}$ cm^2/sec the Reynolds number $Re_r = u^x h_r/\nu$ reaches its critical value [3].

Such a calculation of the roughness index at which the flow becomes turbulent or transitional is, naturally, difficult and to some extent tentative when based on model or prototype tests. Nevertheless, with the proper use of the formulas and the concepts presented here, it is possible to expedite the optimization of mass transfer processes in reactors of the given kind.

An application of these relations to cases where not only hydrodynamic but also other factors play a role requires certain restrictive stipulations. In electrochemical systems, for example, within the cell cavity between anode and cathode there act electrostatic forces which cause a migration of ions on top of diffusion. Under certain conditions, however (sufficiently high concentration of "extraneous" electrolyte [3]), this effect of ion migration may be disregarded and the problem can be solved as a purely hydrodynamic one.

NOTATION

a is a constant coefficient;
c is the concentration of reactant or product;
D is the diffusivity;
d is the channel (tube, chamber) diameter;
j is the diffusion current;
h is the channel (chamber, asperity) height;
K is a constant coefficient;
m is the power exponent;
R is the channel radius;
Re is the Reynolds number;
u is the flow velocity;
Pr is the Prandtl number;
x is the longitudinal coordinate;
y is the transverse coordinate;
δ is the thickness of the boundary layer;
ν is the kinematic viscosity;
τ is the shearing stress;
ρ is the density.

Subscripts

0 refers to the entrance section of a channel or to the channel axis;
v refers to the viscous (laminar) sublayer;
h refers to the hydrodynamic boundary layer;
d refers to the diffusion boundary layer;
e denotes the equivalent (radius);
r refers to roughness;
i denotes the i-th channel segment or the i-th reactant, etc.;
b refers to the boundary;
s refers to the surface.

A bar denotes the mean value of the given quantity.

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