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UNSTEADY MASS TRANSFER OF SPHERICAL PARTICLES

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A one-dimensional problem on unsteady diffusion of a distributed substance through a conventional diffusion boundary layer is formulated and solved. Based on its solution relations are obtained for calculation of the instantaneous and mean mass transfer coefficients for the times corresponding to layer formation. A procedure is proposed for calculation of the mentioned coefficients using the known dimensionless relations derived for the steady process.

Introduction. In calculations of mass transfer between dispersed and continuous phases in various mass transfer processes as well as in chemical interactions controlled by mass transfer in the ambient phase, use is usually made of dimensionless relations that have been derived in a steady-state regime and are valid for these conditions. At the same time in practice cases occur in liquid–liquid, liquid–solid, gas–liquid systems when mass transfer is an unsteady process, namely, at low values of the diffusion coefficient and when the contact times of interacting phases are small. The approach proposed below is intended for describing such mass transfer processes.

Mathematical Model. Consider a particle of the dispersed phase and assume that it represents a sphere. In the general case, a flow around a spherical particle is characterized by complicated hydrodynamics [1], which makes it difficult to obtain an exact analytical solution allowing for peculiarities of the flow over the sphere surface, inhomogeneity of the viscosity and velocity fields, and the diffusion coefficient in dynamic and diffusional boundary layers. Therefore, in order to simplify the problem we introduce a diffusional boundary layer with thickness δ = const and spherical symmetry which corresponds to the condition of equality of the diffusion resistance of mass transfer at $\tau \to \infty$ to that in the steady state: $R_\beta = 1/\beta_{\rm st}$.

Assume that: 1) distributed-substance transfer in this boundary layer is accomplished only by molecular diffusion at D = const; 2) particle size remains unchanged through the process; 3) the substance concentration at the external boundary of the boundary layer is constant and equal to its value in the flow core: $C_{\rm med}$ = const; 4) the initial concentration of the substance in the boundary layer is also constant and equal to $C_{\rm med}$; 5) near the particle surface the equilibrium concentration is reached momentarily and is constant through the process: $C_{\rm s}$ = const; 6) the problem possesses spherical symmetry.

With such assumptions made, we formulate a nonstationary problem of diffusion of a distributed substance in the conventional boundary layer in the form:

$$\frac{\partial C}{\partial \tau} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right), \quad R < r < R + \delta, \quad \tau > 0;$$

$$C|_{\tau=0} = C_{\rm med}, \quad R \le r \le R + \delta;$$

$$C|_{r=R} = C_{\rm s}, \quad \tau > 0;$$

$$C|_{r=R+\delta} = C_{\rm med}, \quad \tau > 0, \tag{1}$$

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where D, C_{med}, C_s, R, $\delta = \text{const}$.

To solve (1) analytically, we perform substitution of the variables in (1) using the relations: $\rho = r/R$; $\delta_0 = \delta/R$; $W(\rho, \text{Fo}_m) = [C(r, \tau) - C_{\text{med}}]/(C_s - C_{\text{med}})$; $\text{Fo}_m = D\tau/R^2$

$$\frac{\partial W}{\partial \text{Fo}_m} = \frac{\partial^2 W}{\partial \rho^2} + \frac{2}{\rho}\frac{\partial W}{\partial \rho}, \quad 1 < \rho < 1 + \delta_0, \quad \text{Fo}_m > 0; \tag{2}$$

$$W|_{\text{Fo}_m=0} = 0, \quad 1 \le \rho \le 1 + \delta_0;$$

$$W|_{\rho=1} = 1, \quad \text{Fo}_m > 0;$$

$$W|_{\rho=1+\delta_0} = 0.$$

Using the integral transform for a hollow sphere in the form [2]

$$\overline{W}(n, \text{Fo}_m) = \int_1^{1+\delta_0} \rho W(\rho, \text{Fo}_m) \sin\frac{n\pi(\rho - 1)}{\delta_0}\, d\rho, \tag{3}$$

we find the inverted transform of the operator

$$\int_1^{1+\delta_0} \rho \left(\frac{\partial^2 W}{\partial \rho^2} + \frac{2}{\rho}\frac{\partial W}{\partial \rho}\right) \sin\frac{n\pi(\rho - 1)}{\delta_0}\, d\rho = \frac{n\pi}{\delta_0} - \left(\frac{n\pi}{\delta_0}\right)^2 \overline{W}. \tag{4}$$

With allowance for (4) we can write problem (2) in the following way:

$$\frac{d\overline{W}}{d\text{Fo}_m} + \left(\frac{n\pi}{\delta_0}\right)^2 \overline{W} = \frac{n\pi}{\delta_0}, \quad \text{Fo}_m > 0, \quad \overline{W}|_{\text{Fo}_m=0} = 0. \tag{5}$$

A solution of (5) is

$$\overline{W}(n, \text{Fo}_m) = \frac{\delta_0}{n\pi}\left[1 - \exp\left[-\left(\frac{n\pi}{\delta_0}\right)^2 \text{Fo}_m\right]\right]. \tag{6}$$

Using the inversion formula [2]

$$W(\rho, \text{Fo}_m) = \frac{2}{\rho\delta_0}\sum_{n=1}^{\infty} \overline{W}(n, \text{Fo}_m) \sin\frac{n\pi(\rho - 1)}{\delta_0}, \tag{7}$$

we pass from (6) to a solution of the problem in the space of inverted transforms

$$\frac{C(r, \tau) - C_{\text{med}}}{C_s - C_{\text{med}}} = \frac{2}{\pi\rho}\sum_{n=1}^{\infty} \frac{1}{n} \sin\frac{n\pi(\rho - 1)}{\delta_0}\left[1 - \exp\left[-\left(\frac{n\pi}{\delta_0}\right)^2 \text{Fo}_m\right]\right]. \tag{8}$$

To improve this solution, we use the procedure described in [3]. For this, we add the expression $(1/\rho_0)((1 + \delta_0)/\rho - 1)$ to the right-hand side and subtract $(2/n\rho)\sum_{n=1}^{\infty}(1/n)\sin n\pi(\rho - 1)/\delta_0$, which is equal to it. As a result, we arrive at

$$\frac{C(r, \tau) - C_{\text{med}}}{C_s - C_{\text{med}}} = -\frac{2}{\pi\rho}\sum_{n=1}^{\infty} \frac{1}{n} \sin\frac{n\pi(\rho - 1)}{\delta_0} \exp\left[-\left(\frac{n\pi}{\delta_0}\right)^2 \text{Fo}_m\right] + \frac{1}{\delta_0}\left(\frac{1 + \delta_0}{\rho} - 1\right). \tag{9}$$

Next, using the equality

$$i(\tau) = -D\left.\frac{\partial C}{\partial r}\right|_{r=R} = \beta(\tau)(C_s - C_{\text{med}}), \tag{10}$$

where $i(\tau)$ is the specific flow of the distributed substance near the spherical particle surface (kg/(m^2·sec)), we calculate the instantaneous mass transfer coefficient from the solution obtained

$$\beta(\tau) = \frac{-D\left.\frac{\partial C}{\partial r}\right|_{r=R}}{C_s - C_{\text{med}}}. \tag{11}$$

As a result, we have

$$\beta(\tau) = \frac{[(1+\delta_0)/\delta_0]\,D}{R} + \frac{2D}{\delta}\sum_{n=1}^{\infty}\exp\left[-\left(\frac{n\pi\sqrt{D}}{\delta}\right)^2\tau\right]. \tag{12}$$

Note that at $\tau \to \infty$ and $\delta \to \infty$ this equation yields $\beta(2R)/D = \text{Nu}_{\text{m.st.min}} = 2$, which corresponds to steady-state diffusion in a stationary medium [4].

Now we determine the mean value of $\beta(\tau)$ on the segment $[0, \tau_0]$, where τ_0 is the time of contact of phases:

$$\bar{\beta}(\tau_0) = \frac{1}{\tau_0}\int_0^{\tau_0}\beta(\tau)\,d\tau. \tag{13}$$

Considering that $\sum_{n=1}^{\infty} 1/n^2 = \pi^2/6$, we obtain from (12)

$$\bar{\beta}(\tau_0) = \frac{[(1+\delta_0)/\delta_0]\,D}{R} + \frac{\delta_0}{3\tau_0} - \frac{2\delta_0}{\pi^2\tau_0}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left[-\left(\frac{n\pi\sqrt{D}}{\delta_0}\right)^2\tau_0\right]. \tag{14}$$

Using Eq. (14) and considering that the series converges rapidly (~ as $\Sigma\, 1/n^2$) we can finally write

$$\overline{\text{Nu}}_{\text{m.un}} = 2\frac{1+\delta_0}{\delta_0} + \frac{\delta_0}{\text{Fo}_\text{m}}\left[\frac{2}{3} - \frac{4}{\pi^2}\exp\left(-\pi^2\frac{\text{Fo}_\text{m}}{\delta_0^2}\right)\right], \tag{15}$$

where $\overline{\text{Nu}}_{\text{m.un}} = \bar{\beta}(2R)/D$ represents $\overline{\text{Nu}}_\text{m}$ on the segment $[0, \tau_0]$.

At $\text{Fo}_\text{m} \to \infty$ we obtain from (15)

$$\lim \overline{\text{Nu}}_{\text{m.un}} = \text{Nu}_{\text{m.st}} = 2\frac{1+\delta_0}{\delta_0} \tag{16}$$

is the steady-state Nu_m corresponding to the hydrodynamical situation determining the thickness of the conventional diffusion boundary layer δ_0. At $\delta_0 = \delta/R \to \infty$, which corresponds to diffusion in a steady-state medium, the limiting case for Nu_m, i.e., $\text{Nu}_{\text{m.st.min}} = 2$, follows again from (16), which corresponds to the analytical solution of the problem for steady-state diffusion [4].

With allowance for (16) we can represent Eq. (15) in the form

$$\overline{\text{Nu}}_{\text{m.un}} = \text{Nu}_{\text{m.st}} + \frac{\delta_0}{\text{Fo}_\text{m}}\left[\frac{2}{3} - \frac{4}{\pi^2}\exp\left(-\pi^2\frac{\text{Fo}_\text{m}}{\delta_0^2}\right)\right]. \tag{17}$$

Equation (17) is used to calculate mean mass transfer coefficients on the segment $[0, \tau_0]$ for unsteady mass transfer processes. The procedure for its application is as follows: 1) $\text{Nu}_{\text{m.st}}$ is calculated for the mass transfer

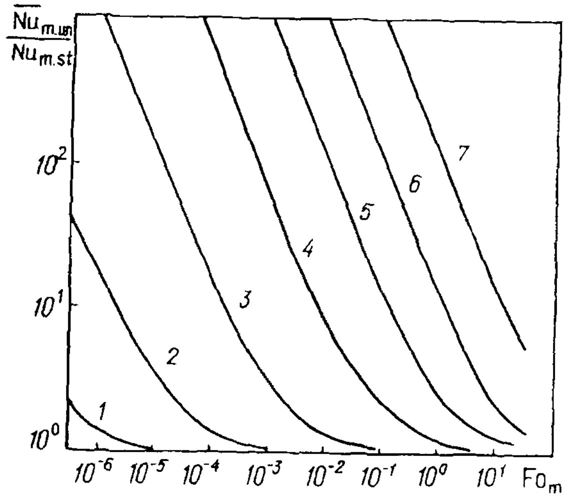

Fig. 1. $\overline{\text{Nu}}_{m.n}/\text{Nu}_{m.st} = f(\text{Fo}_m)_{\delta_0}$ calculated by Eq. (17): 1) $\delta_0 = 0.001$, 2) 0.01, 3) 0.1, 4) 1, 5) 10, 6) 100, 7) 1000.

conditions using the corresponding dimensionless mass transfer equation; 2) using (16), the nominal thickness of the diffusion boundary layer δ_0 corresponding to the determined $\text{Nu}_{m.st}$ is found: $\delta_0 = 2/(\text{Nu}_{m.st} - 2)$; 3) with the aid of Eq. (17), the running mean $\overline{\text{Nu}}_{m.un}$ number on the segment $[0, \tau_0]$ and then the mean mass transfer coefficient on it are determined: $\bar{\beta}_{un} = \overline{\text{Nu}}_{m.un}D/2R$.

Figure 1 shows $\overline{\text{Nu}}_{m.un}/\text{Nu}_{m.st} = f(\text{Fo}_m)_{\delta_0}$ calculated at different δ_0 values.

At $\text{Fo}_m \to 0$, $\bar{\beta}_{un} \to \infty$, which corresponds to an infinitely high concentration gradient near the interphase at the onset of mass transfer. As far as the process develops, the concentration gradient decreases thus resulting, in conformity with (11) and (13), in a decrease in $\bar{\beta}_{un}$, which tends at $\tau \to \infty$ to its limiting (stationary) value for the prescribed hydrodynamic conditions of the flow around the particle.

As is seen, the Fo_m value at which the function $\overline{\text{Nu}}_{m.un}$ approaches its stationary value with a prescribed accuracy depends to a large extent on δ_0, which is determined by the particle diameter $2R$ and hydrodynamic conditions of the flow past the particle, which determine the value of δ. The ratio $\bar{\beta}_{un}/\beta_{st}$ increases with an increase in the nominal thickness of the diffusional boundary layer δ and particle diameter $2R$ and with a decrease in the diffusion coefficient D and the time of interaction of phases τ_0.

Now we illustrate Eq. (11) as applied to an analysis of the unsteadiness effect on mass transfer in various mass transfer processes.

Analysis of Mass Transfer Processes. 1. *Drying.* Fast drying processes are typical for spray driers, pneumatic, cyclone driers, and some others. Calculations based on data [5-7] typical for such types of apparatuses on the residence times in the working zone and particle sizes using the known dimensionless equations for mass transfer coefficients show because of the high diffusion coefficient of vapors in gases with the order $O(D) = 10^{-5}$ m^2/sec that at a sufficiently high relative velocity of particles under drying conditions large Fo_m values and, as a consequence, a steady mass transfer process are realized.

However, at $\text{Re}_{rel} \to 0$ the situation can be different since under these conditions the parameter δ_0 increases considerably which, as is seen from the figure, entails marked expansion of the region where the unsteadiness effect is manifested. For instance, on evaporation of water droplets with diameter $2R = 3.2$ mm in air at a relative velocity of the phases equal to zero for the experimental conditions described in [8] the $\text{Nu}_{m.st}$ calculation performed by the procedure [9] with allowance for natural convection and Stefan diffusion phenomena gives $\text{Nu}_{m.st} = 2.59$, to which, according to Eqs. (16) and (17), $\delta_0 = 3.4$ and $\overline{\text{Nu}}_{m.un} = 3.46$ correspond, i.e., the increase in the mass transfer coefficient due to the unsteadiness effect is 34%.

It should be also noted that the Nu_m values observed in [8] are higher than those calculated above, which, in our opinion, is due to turbulence in an air flow that moved, instead of remaining motionless, through the channel with mean velocity $v = 3.785$ m/sec, which for channel diameter $d_c = 0.048$ m gives $\text{Re} = vd_c/\nu = 12{,}275 > 10{,}000$.

Vortices generated by the turbulent motion of air that has penetrated into the outer region of the diffusional boundary layer existing around a droplet and diffused it, thus causing a decrease in its effective thickness and, consequently, an increase in the $\mathrm{Nu_m}$ number. The analysis made confirms the conclusion [10] that a use of formulas of the type

$$\mathrm{Nu_m} = 2 + A\,\mathrm{Re}^m\,\mathrm{Pr}_\mathrm{m}^n \tag{18}$$

at $\mathrm{Re_{rel}} \to 0$ is doubtful. Indeed, in this case empirical formula (18) gives $\mathrm{Nu_m} = 2$; however, for nonlaminar motion of the external phase $\mathrm{Nu_m}$ must not be equal to 2 (which corresponds to molecular diffusion in a steady-state medium) but, in accordance with (16), to the value of $\mathrm{Nu_{m.st}} = 2(1 + \delta_0)/\delta_0 > 2$, where δ_0 is determined by the degree of turbulence of the flow of the external phase, which is dependent at $\mathrm{Re_{rel}} \to 0$ on $\mathrm{Re} = vd_c/\nu$, where v is the absolute velocity of the external phase. Moreover, the influence of the natural convection and Stefan diffusion (of the latter, by the way, at any values of $\mathrm{Re_{rel}}$) on mass transfer must be taken into consideration.

2. *Liquid Extraction.* The diffusion coefficients of low-molecular substances in liquids are smaller by four orders of magnitude than in gases, i.e., $O(D) = 10^{-9}$ m^2/sec. Nevertheless, calculations for mass transfer in a continuous phase with extraction in a column apparatus with sieve trays at the parameters values typical for this apparatus [11] show a small contribution of the unsteadiness effect which in practice can be neglected.

3. *Absorption.* Though the diffusion coefficients of an absorbed gas in a liquid phase are of the same order of magnitude as in the previous case, due to the smaller time of contact of the phases in the bubbling layer the unsteadiness effect can be rather considerable in some cases. Thus, for the conditions [12] of SO_2 absorption in water the mass transfer coefficient in the liquid is reported to be equal to $\beta = 1.5 \cdot 10^{-4}$ m/sec. If it is assumed for sieve trays that the height of the bubbling layer is $h = 0.05$ m, the bubble diameter is $d = 0.005$ m, the speed of its rise is $v = 0.25$ m/sec, the coefficient of SO_2 diffusion in water at 20°C is $D = 1.3 \cdot 10^{-9}$ m^2/sec, then the corresponding calculations give: $\mathrm{Nu_{m.st}} = 577$; $\overline{\mathrm{Nu}}_\mathrm{m.un} = 801$, i.e., the unsteadiness effect causes an increase in the mass transfer coefficient by 39%.

4. *Dissolution of Solid Substances.* In dissolution of solid substances, cases are often encountered when mass transfer proceeds in unsteady conditions caused, for instance, by particle residence in a flow changing its direction or velocity or particle migration from one flow to another differing from the former in the velocity vector [1], and so on. The characteristic times of these transient processes are sufficiently small, which makes Eq. (17) applicable for their description.

In particular, among fast unsteady processes is dissolution of solid substances exposed to pulsed attacks for the purpose of process intensification, which are generated in a liquid at very high (explosive) rates of energy transformation or conversion [1]. If it is assumed that the diffusional boundary layer undergoes restoration at the moment of pulsed action, then with knowledge of the pulse period τ_0 one can calculate the mass transfer rate by relation (17).

5. *Chemical Reactions.* All the above gives us grounds to assert that the results obtained can be also applied for describing the kinetics of chemical reactions in heterogeneous systems in which the continuous phase is a liquid and the rate of the process is limited by mass transfer in the liquid phase.

6. *Mass Transfer at Lower Temperatures.* With a decrease in the system's temperature the diffusion coefficient of the distributed substance decreases, which, other conditions being equal, results in enhancement of the unsteadiness effect. In connection with this, at temperatures lower than 0°C it should be expected that this effect can exert a pronounced influence on mass transfer in the liquid phase under conditions of short-time contact of phases.

7. *Diffusion Processes in Polymer Systems.* The diffusion coefficients of macromolecules in monomer solutions are of the order of $O(D) = 10^{-10} \ldots 10^{-13}$ m^2/sec [13], which at small times of contact of the phases makes the unsteadiness effect even more considerable than in the cases above.

CONCLUSIONS

1. As a result of solving the diffusion problem for a distributed substance in a conventional boundary layer, equations for calculation of instantaneous and time-averaged mass transfer coefficients as well as an expression relating the mass-transfer Nusselt numbers for unsteady and steady stages of the process are obtained.

2. A procedure is proposed for calculation of the mass transfer coefficient in the unsteady stage of the process by the dimensionless equations obtained under steady mass transfer conditions.

3. Based on the relations obtained, the unsteadiness effect is analyzed in various mass transfer processes, which allows the regions of its most pronounced influence to be found.

4. It is shown that at zero relative velocity of the continuous and dispersed phases the mass-transfer Nusselt number must not be assumed equal to 2 in calculations if their absolute velocities are not zero. For this case, it is suggested to take also into account the influence of the Reynolds number, calculated in terms of the absolute velocity of the continuous phase, on mass transfer.

NOTATION

C, concentration, kg/m^3; D, diffusion coefficient, m^2/sec; r, radial coordinate, m; R, radius of spherical particle, m; v, velocity, m/sec; $v_{\rm rel}$, relative velocity of phases, m/sec; β, mass transfer coefficient, m/sec; δ, thickness of conventional diffusional boundary layer, m; ν kinematic viscosity, m^2/sec; τ, time, sec; $\mathrm{Fo_m} = D\tau_0/R^2$, mass-transfer Fourier number; $\mathrm{Nu_m} = \beta(2R)/D$, mass-transfer Nusselt number; $\mathrm{Pr_m} = \nu/D$, mass-transfer Prandtl number; $\mathrm{Re_{rel}} = v_{\rm rel}(2R)/\nu$, Reynolds number. Subscripts: c, channel; un, unsteady; rel., relative; s, at the particle surface; med, ambient medium; st, steady; m, mass-transfer.

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