CERTAIN PROBLEMS WITH THE APPLICATION OF STOCHASTIC DIFFUSION PROCESSES FOR THE DESCRIPTION OF CHEMICAL ENGINEERING PHENOMENA. FORMULATION OF BOUNDARY CONDITIONS IN FLOW SYSTEMS

Vladimir KUDRNA[a], Pavel HASAL[a] and Libor VEJMOLA[b]

[a] *Department of Chemical Engineering, Prague Institute of Chemical Technology, 166 28 Prague 6, The Czech Republic*
[b] *OIS SPOLANA Inc., 277 11 Neratovice, The Czech Republic*

Received January 20, 1993
Accepted April 26, 1993

Problems associated with the formulation of the boundary conditions for diffusion equations describing flow-through chemical-engineering systems from the point of view of stochastic process theory are discussed. An approach to modelling such systems is presented, allowing the one-dimensional diffusion (dispersion) model of a continuous flow mixer, commonly used in chemical engineering, to be reassessed from a rather general point of view.

In our previous papers[1 – 3] we discussed some problems related to two ways of formulating the diffusion equation: the conventional approach and the so called probabilistic approach. The possibility of modelling diffusion processes by means of adequate stochastic differential equations[2,3] has also been mentioned. Major attention has been paid to stochastic diffusion processes occurring in the three-dimensional unbounded Euclidean space. However, an actual chemical-engineering equipment must be looked upon as a bounded part of this space only, defined by its boundaries, which are of various kinds (e.g. permeable, reflecting, and absorbing boundaries). Each kind of system boundary requires a specific mathematical formulation of the boundary condition. Nevertheless, there are some differences between the probabilistic and classical approaches which are in a sense similar to problems encountered when the diffusion equation itself is to be formulated.

An exhaustive analysis of the boundary conditions of diffusion equations has been performed by Feller[4,5] and Bharucha-Reid[6], who divided the boundaries into several groups, including processes with discontinuous trajectories. This approach has also been applied to multidimensional problems; for instance, a very simple classification of the diffusion processes and their boundary conditions can be obtained by using the so called characteristic operator, defined and introduced by Dynkin[7].

Gardiner[8], who applied this classification to processes dealt with by natural sciences, pointed out that only two kinds of boundaries are actually of importance: the reflecting boundary and the absorbing boundary; a combination of these two boundaries, the so called elastic boundary, is occasionally used as well. Somewhat different boundary conditions are used in literature dealing with partial differential equations[9]:

a) Boundary conditions of the first kind (Dirichlet's boundary conditions), prescribing value of PDE solution at the boundaries, e.g. temperature or concentration of species on the surface of the spatial region.

b) Boundary conditions of the second kind (Neumann's boundary conditions), prescribing the flux of the quantity under consideration through the surface, e.g. heat or mass flux.

c) Boundary conditions of the third kind (Newton's boundary conditions), which are linear combinations of the conditions of the first and second kinds.

Application of such general mathematical theories to the solution of some chemical-engineering problems, where significant simplifications are commonly adopted, is often associated with serious difficulties. The so called Danckwert's boundary conditions[10] for flow-through mixers and reactors are a typical example. A mixer is considered a one-dimensional system, with a step change in the diffusion coefficient occurring at the two boundaries. This model has been subject to extensive discussion, and reviews on this topic can be found in some chemical engineering monographs[11,12].

Let us consider a flow-through "closed–closed" system (cf. e.g., ref.[12]) depicted in Fig. 1, through which an incompressible liquid flows and carries a detectable and reacting component A. Suppose that the concentration field of component A inside the system can be described, with a sufficient accuracy, by the equation

$$\frac{\partial \rho_A}{\partial t} + v\frac{\partial \rho_A}{\partial x} - D\frac{\partial^2 \rho_A}{\partial x^2} + r(\rho_A) = 0\,, \qquad 0 \le x \le L\,, \tag{1}$$

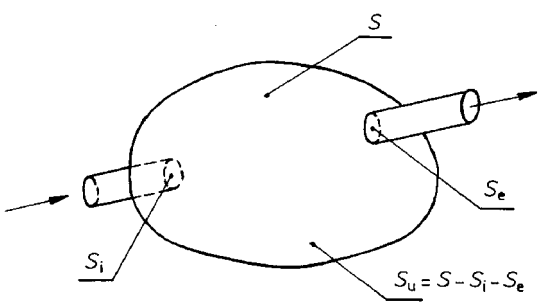

FIG. 1
An one-dimensional flow-through system

where v is the velocity of the liquid, D is the diffusion coefficient of component A and r is the reaction rate. This equation implies that changes in the component concentration ρ_A are only significant in the direction of the x-axis and in time ($\rho_A = \rho_A(x,t)$). The quantities v and D are supposed to be constant.

Now, it is necessary to specify the initial condition, i.e. the initial distribution of concentration along the reactor:

$$\lim_{t \to 0} \rho_A(x,t) = \rho_{A0}(x) . \tag{2}$$

Furthermore, two boundary conditions are necessary, because Eq. (*2*) is second order with respect to x. These conditions can have the form

$$\lim_{x \to 0-} v\, \rho_A(x,t) = \lim_{x \to 0+} \left[v\, \rho_A(x,t) - D \frac{\partial \rho_A(x,t)}{\partial x} \right] \tag{3}$$

$$\lim_{x \to L} \frac{\partial \rho_A(x,t)}{\partial x} = 0 . \tag{4}$$

Danckwerts[10] formulated these boundary conditions for the steady state and for a first order chemical reaction. Actually, this formulation was used earlier by Langmuir (cf. e.g.[11]). The boundary conditions (*3*) and (*4*) imply the occurrence of plug flow in both the inlet and outlet connecting pipes; hence, the following relation holds true:

$$D = 0 , \qquad x < 0 \cup x > L . \tag{5}$$

Equations (*3*) and (*4*) have been proved to apply to the unsteady state[13,14] and nonlinear reaction kinetics[15] as well. Another system of boundary conditions preserving the continuity of concentrations and fluxes of components at the boundaries have also been suggested[16]. It should be noted that for the reactor design, the two conditions are required at the reactor inlet only.

It must be emphasized that the discontinuity of the diffusion coefficient at the ends of the reactor brings about discontinuity of the solution of the diffusion equation. Furthermore, the boundary condition at the reactor outlet is corrupted in the important case of plug flow inside the reactor, or in the case of a real short reactor and a nonzero D value.

It is noteworthy that stochastic process theory can deal with problems involving diffusion coefficients which are discontinuous in space (see, e.g., ref.[17]). A method solving this kind of problem by means of an adequately defined integral operator has been suggested[18,19], this method, however, is only suitable for addressing linear problems. Attempts have been made to use diffusion coefficients which are also continuous at the reactor boundaries[20 – 22].

Dilman and Kronberg[23 – 25] derived a model which partly eliminates the basic shortcomings of the diffusion model: they introduced a concept of process relaxation time, within which the flux of the detectable component can be defined as another independent variable in addition to the concentration, and, in some cases, the diffusion coefficient can be neglected altogether. This model allows both the concentration and the flux of the component at the inlet of the reactor to be prescribed.

The following text proposes a three-dimensional diffusion model of a flow mixer and gives a formulation of the corresponding stochastic differential equation (SDE). This model allows the problems of formulation of boundary conditions for flow mixers and chemical reactors to be discussed from a rather general point of view. The applicability of this approach to stochastic modelling of continuous mixers and chemical reactors is also discussed.

THEORETICAL

Consider a bounded region of space Ω_R completely filled with a flowing liquid. The region is confined by surface S in which there are two openings: the liquid can only flow in through the one and out through the other (Fig. 2). The openings are connected to pipes which have impermeable walls and connect the region Ω_R to the environment. Molecules of the diffusing, and in the chemical reactor also reacting, component A move together with the liquid through the spatial region considered (this component A serves as a tracer, which can be detected, e.g. by its colour or electrical conductivity).

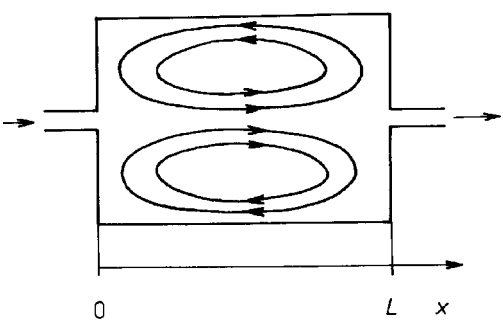

FIG. 2
Bounded region of space Ω_R with impermeable surface $S_u = S - S_i - S_e$

Denote the area of the inlet opening as S_i and the area of the outlet opening as S_e. The surface $S_u = S - S_i - S_e$ is impermeable both for the liquid and for the diffusing molecules.

Obviously, it is feasible to consider the boundary conditions for both the carrier liquid and the diffusing component over the impermeable surface only. Inside the pipes connecting the liquid region Ω_R to the environment, the motion of both the liquid and component A has to be described by equations of motion (momentum balances). However, the description of the flow pattern is usually replaced by adequate boundary conditions at the two openings.

The spatial and time distribution of component A is described by means of the mass balance

$$\frac{\partial \rho_A}{\partial t} + \nabla . (\boldsymbol{v}\, \rho_A) - \nabla . (\boldsymbol{D} . \nabla \rho_A) = 0 . \qquad (6)$$

It has been demonstrated previously[1] that Eq. (*6*) is also applicable to the spatial distribution of component A in the case of a turbulent flow, where the concentration ρ_A and the velocity of the flowing liquid $\boldsymbol{v}$ must be time-averaged. The quantity $\boldsymbol{D}$ then represents the sum of the turbulent and molecular diffusivities: this can be expressed as

$$\boldsymbol{D} = \boldsymbol{D}_T + D\, \boldsymbol{I} , \qquad (7)$$

where $\boldsymbol{D}_T$ is the turbulent diffusivity, D is the molecular diffusivity regarded as a scalar constant, and $\boldsymbol{I}$ is the identity tensor. The diffusivity $\boldsymbol{D}$ is, in general, a symmetric tensor of the second order; its matrix is positively definite. The diffusivities $\boldsymbol{D}$, $\boldsymbol{D}_T$ and D are, in general, functions of time t and of the spatial position, expressed by means of the position vector $\boldsymbol{x}$. The vector

$$\boldsymbol{q}(\boldsymbol{x},t) = \boldsymbol{v}\, \rho_A - \boldsymbol{D} . \nabla \rho_A \qquad (8)$$

is the flux intensity of component A at time t and position $\boldsymbol{x}$. The heat transfer equation[1] can be written analogously, the liquid temperature being the unknown function and $\boldsymbol{D}$ being the thermal diffusivity tensor. The initial condition for Eq. (*6*) is given by the initial distribution of component A within the region Ω_R, i.e.

$$\lim_{t \to 0} \rho_A(\boldsymbol{x},t) = \rho_{A0}(\boldsymbol{x}) , \qquad \boldsymbol{x} \in \Omega_R . \qquad (9)$$

Before formulating the boundary conditions we will introduce symbols for the position vectors assigned to points on the surface S of the considered region Ω_R (see Fig. 1):

$$\boldsymbol{r}_j = \boldsymbol{x} \in S_j , \qquad j = \{i, e, u\} .$$

Furthermore, we denote a scalar product of any vector $\boldsymbol{b}$ and the unit vector as b_n:

$$b_n = \boldsymbol{b} . \boldsymbol{n} , \qquad \boldsymbol{n} = \boldsymbol{n}(\boldsymbol{r}) ,$$

The following boundary condition then applies to the impermeable part S_u of the total surface of the region Ω_R:

$$\lim_{x_n \to r_n} q_n(x_n,t) = 0 . \qquad (10)$$

We will consider the flux of component A inside the inflow and outflow openings as a continuous function of the spatial coordinate, i.e.

$$\lim_{x_n \to r_{j,n}-} q_n(x_n,t) = \lim_{x_n \to r_{j,n}+} q_n(x_n,t) , \qquad j = \{i, e\} . \qquad (11)$$

Now, we adopt some assumptions concerning the flow pattern inside the equipment modelled:

A1) The concentration of component A is sufficiently low for the flow pattern to be unaffected by its presence.

A2) The flow of the liquid is quasistationary.

A3) The structure of the diffusion tensor in a proximity to the impermeable wall is such that the direction of one of its eigenvectors is identical with that of the surface normal at the given point on the wall (surface S_u).

The first two assumptions have obvious physical interpretation. Assumption *A2*) further demands that the velocity $\boldsymbol{v}$ and diffusivity $\boldsymbol{D}$ are functions of the position in space only, not of time. Assumption *A3*) expresses the fact that near the surface, the diffusion in the direction perpendicular to the surface differs significantly from that in the tangential direction. The diffusion fluxes in these two directions are the prevailing ones. It can be proved that for a symmetrical second order tensor $\boldsymbol{T}$ there exists a vector $\boldsymbol{r}$ such that $\boldsymbol{r} . \boldsymbol{T} = \lambda \boldsymbol{r}$, where λ is an eigenvalue of $\boldsymbol{T}$ (see, e.g., ref.[26]). Assumption *A3*) can be thus formulated as

$$\lim_{\boldsymbol{x}\to\boldsymbol{r}} \boldsymbol{n}(\boldsymbol{r}) \,.\, \boldsymbol{D}(\boldsymbol{x}) \,.\, \nabla\, \rho_{\mathrm{A}}(\boldsymbol{x},t) \;=\; \lim_{\boldsymbol{x}\to\boldsymbol{r}} \boldsymbol{n}(\boldsymbol{r}) \,.\, D(\boldsymbol{x})\, \nabla\, \rho_{\mathrm{A}}(\boldsymbol{x},t) \;=$$

$$= \lim_{\boldsymbol{x}\to\boldsymbol{r}} D(x_{\mathrm{n}}) \nabla_{\mathrm{n}}\, \rho_{\mathrm{A}}(x_{\mathrm{n}},t)\,, \qquad \boldsymbol{r} \in S_{\mathrm{u}}\,, \tag{12}$$

where $D(\boldsymbol{x})$ denotes an eigenvalue of $\boldsymbol{D}$ in the limiting case where $\boldsymbol{x}$ approaches a point $\boldsymbol{r}$ located on the impermeable surface, $\boldsymbol{r} \in S_{\mathrm{u}}$. This eigenvalue can be, naturally, a function of the spatial coordinate. The symbol $\nabla_{\mathrm{n}}\, \rho_{\mathrm{A}} = \partial \rho_{\mathrm{A}} / \partial n$ denotes the concentration gradient of component A in the direction of the external normal at the given position of the space. An analogous relation holds for the points located within the inlet and outlet opening areas. The direction of the first eigenvector is parallel to the axes of the pipes. The other two are directed towards the walls of the pipes attached to the openings (inside the pipes with circular cross-sections, however, the directions of the eigenvectors are ambiguous). Combining Eqs (*8*) and (*10*) and including assumptions *A1*) through *A3*) we obtain

$$\lim_{x_{\mathrm{n}}\to r_{\mathrm{n}}} v_{\mathrm{n}}\, \rho_{\mathrm{A}}(x_{\mathrm{n}},t) \;-\; D(x_{\mathrm{n}}) \nabla_{\mathrm{n}}\, \rho_{\mathrm{A}}(x_{\mathrm{n}},t) \;=\; 0\,, \qquad r_{\mathrm{n}} \in S_{\mathrm{u}}\,. \tag{13}$$

Due to the impermeability of the surface S_{u}, the normal component of the fluid velocity $\boldsymbol{v}$ must also converge to zero (by virtue of assumption *A1*)):

$$\lim_{x_{\mathrm{n}}\to r_{\mathrm{n}}} \frac{\partial \rho_{\mathrm{A}}(x_{\mathrm{n}},t)}{\partial n} \;=\; 0\,, \qquad r_{\mathrm{n}} \in S_{\mathrm{u}}\,. \tag{14}$$

In the case of a semipermeable wall, i.e. a wall permeable for molecules of component A only, this equation must be replaced with a more complex equation (boundary condition of the third kind), viz.

$$\frac{\partial \rho_{\mathrm{A}}(x_{\mathrm{n}},t)}{\partial n} \;=\; C_1\, \rho_{\mathrm{A}} \;+\; C_2\,, \qquad x_{\mathrm{n}} \to r_{\mathrm{n}} \in S_{\mathrm{u}}\,, \tag{15}$$

in which the coefficients C_1 and C_2 are, in general, functions of r_{n}. Equation (*15*) is also applicable if temperature is considered instead of the concentration of component A and the wall is assumed to be imperfectly heat insulated.

In analogy with Eq. (*11*) it follows that both the concentration of component A and its gradient are continuous functions of the spatial coordinate at the inlet and outlet openings, assuming that the coefficients $\boldsymbol{v}$ and $\boldsymbol{D}$ are continuous there as well:

$$\lim_{x_n \to r_{j,n}-} \rho_A(x_n,t) = \lim_{x_n \to r_{j,n}+} \rho_A(x_n,t) ,$$

$$\lim_{x_n \to r_{j,n}-} \frac{\partial \rho_A(x_n,t)}{\partial n} = \lim_{x_n \to r_{j,n}+} \frac{\partial \rho_A(x_n,t)}{\partial n} , \qquad (16)$$

$$r_{j,n} \in S_j , \qquad j = \{i, e\} .$$

Thus, both the concentration of component A and its derivative can be regarded as the boundary conditions along with Eq. (*14*). If the quantities $\boldsymbol{v}$ and $\boldsymbol{D}$ in Eq. (*6*) are also defined inside the pipes, the boundary conditions (*16*) can be omitted. From the point of view of physical feasibility it is evident that only the boundary condition for the inlet opening must be specified.

Now we will compare the above relations with those provided by stochastic process theory. It is well known that the probability density function[1] characterizing the random motion of a single particle (e.g. molecule) of component A can also be obtained by solving Eq. (*6*). Random motion of the particle can be described in an adequate way by means of the stochastic differential equation[2,8]

$$d\boldsymbol{X}(t) = \boldsymbol{v}[\boldsymbol{X}(t)]dt + \sqrt{2}\,\boldsymbol{G}[\boldsymbol{X}(t)] \,.\, d\boldsymbol{W}(t) , \qquad (17)$$

where $\boldsymbol{X}(t)$ denotes the position vector of the particle trajectory and the random function $\boldsymbol{W}(t)$ is a Wiener process (see, e.g., ref.[8]). The properties of $\boldsymbol{W}(t)$ have been defined previously[2] in a way which is well suited to treating the problem in question. The tensor $\boldsymbol{G}$ (so called stochastic tensor) obeys the following relation[3]:

$$\boldsymbol{D}(\boldsymbol{x}) = 2\boldsymbol{G}(\boldsymbol{x}) \,.\, \boldsymbol{G}^{+}(\boldsymbol{x}) , \qquad (18)$$

where the matrix of tensor $\boldsymbol{G}^{+}$ is the transpose of the matrix of tensor $\boldsymbol{G}$. The velocity of the fluid particle, defined conventionally as

$$\boldsymbol{V}(t) = \frac{\mathrm{d}\boldsymbol{X}(t)}{\mathrm{d}t}, \tag{19}$$

cannot be computed using Eq. (*17*) because the time derivative of the Wiener process exceeds all limits at each time instant (see, e.g., ref.[7]); the particle velocity then would approach infinity at each time instant, which is in contradiction to physical reality. This fact, as is well known, is the principal shortcoming of any diffusion model, responsible for the imperfection of modelling real diffusional processes, especially at the initial stage.

Other problems arise from this fact also if the particle is required to leave the region Ω_R once it has reached the outlet opening. In a proximity to this opening, Eq. (*17*) can be modified, after multiplication by the unit vector of the external normal, whose direction is parallel to the outlet pipe axis

$$\mathrm{d}X_n(t) = [v_n(X_n(t))]\mathrm{d}t + [2\,D(X_n(t))]^{1/2}\mathrm{d}W_n(t), \tag{20}$$

$$X_n \to r_{e,n} \in S_e,$$

where D denotes an eigenvalue of the tensor defined by Eq. (*12*). The random ordinates of the Wiener process possess a Gaussian distribution with the mean value equal to zero. The particle thus can return into the region Ω_R via the outlet opening (in the "upstream" direction) irrespective of the magnitude of the fluid velocity (which is, of course, bounded). To account for the fact that, with a probability equal to one, the particle after the first contact with the exit opening will never return into the region in question, the concept of the absorbing barrier has been introduced in stochastic process theory. The following relation holds[5] for the absorbing barrier near the outlet opening:

$$\lim_{x_n \to r_n} D(x_n) \exp\left[-\int_{x \in S_e} \frac{v_n(x_n)}{D(x_n)}\,\mathrm{d}x_n\right] p(x_n,t) = 0, \tag{21}$$

where $p(x,t)$ is the probability density function for the particle position at time t. Equation (*21*) is met if either the diffusivity $D(x)$ at the outlet opening is zero, or the probability density $p(x_n,t)$ is zero. However, in an actual system these conditions may not be fulfilled, in which case the boundary condition (*21*) is inapplicable.

Now it must be pointed out that in general, continuous flow-through systems are beyond the scope of treatment by stochastic process theory. The problems which this

theory deals with are, in the physical sense, associated with random motion of a particle from the interior of the region to its boundaries (see, e.g., ref.[7] – the first passage time problem). This is related with the fact that the probability density function, which is the solution of the diffusion equation, is normalized: the integral of this function cannot be greater than one. This condition may not be met by flow-through systems, where the concentration of the component can increase. Therefore, the boundary condition of the first kind is (even in the case of a batch system) replaced by the absorbing barrier; it is assumed that the probability density function at the boundary of the system can take one value only, viz. zero. The boundary condition of the second kind, however, is identical with the reflecting boundary.

DISCUSSION

The above considerations demonstrate that the conventional as well as the stochastic (probabilistic) approach to the modelling of flow systems is associated with serious problems from the theoretical point of view, arising from the fact that the boundary conditions inside the inlet and outlet openings, assuming discontinuity of the diffusion coefficient, imply discontinuity of the solution of the diffusion equation.

In our opinion, the above difficulties encountered when modelling flow systems basically do not originate from deficiencies in the formulation of the boundary conditions; actually, as mentioned at the beginning of the discussion, they stem from the very principles of the diffusion model itself, which permits unlimited values of the diffusing particle velocity and particle motion in both directions (in the one-dimensional model).

We suggest that the principal drawbacks of the diffusion model can be eliminated, within the framework of the probabilistic treatment of flow systems, by using an equation generating bounded velocity values rather than by using the kinematic equation (*20*). This approach is used in physics (e.g. ref.[8]) because it allows the forces acting upon particles to be described explicitly. Such models can be referred to as dynamic models. A model of this kind has been derived[2] for the three-dimensional Euclidean space; it is considerably more complex than the kinematic model. Furthermore, it is noteworthy that by using suitably chosen terms in the diffusion equation (including the particle velocity), random motion of the diffusing particles in one direction only can also be described. This approach has been discussed[27] and it has been demonstrated that the steady-state velocity distribution obeys the gamma distribution with the reciprocal argument

$$f_v(v) = \frac{(a/v)^{b+1}}{a\,\Gamma(b)} \exp(-a/v)\,, \qquad (22)$$

where $\Gamma(b)$ is the gamma function and a and b are constants. The function $f_v(v)$ is the steady-state solution of the diffusion (Kolmogorov) equation

$$\frac{\partial f_v}{\partial t} + \frac{\partial}{\partial v}[(\alpha - \beta v) f_v] - \frac{\partial^2}{\partial v^2}(\gamma v^2 f_v) = 0, \qquad (23)$$

$$a = \alpha/\gamma, \quad b = \beta/\gamma + 1.$$

In our forthcoming paper[28] this approach using Eqs (*22*) and (*23*) will be discussed in more detail.

Finally, it should be noted that the Danckwert's model can be interpreted making use of Rippin's[29] concept of recirculating flow inside the mixer or reactor (Fig. 2). Assuming that the cross-sections of the connecting pipes are smaller than the cross-section of the reactor, the velocity of the liquid motion within the inlet pipe differs from that in the reactor. The boundary condition (*3*) then can only be adopted supposing that at the reactor axis the fluid moves from the left to the right at a velocity which is roughly equal to the velocity inside the pipes. In the remaining space of the reactor the fluid circulates, the mean axial velocity of the fluid being zero there. The circulating fluid also carries an amount of the diffusing component A through the cross-section of the reactor. This concept enables an interpretation of the step change in concentration at the reactor inlet: The average concentration of the component at the beginning of the reactor is lower than that within the inlet pipe because this component is consumed by a chemical reaction.

The boundary condition (*4*) describes the reverberation of molecules of component A on the impermeable wall at the reactor outlet. If the size of this wall is substantially greater than the cross-section of the outlet opening, then the mean value of the concentration gradient approaches zero, although the gradient inside the pipe itself is nonzero. The boundary condition (*4*) may not be satisfied if Eq. (*1*) describes the heat transfer inside the reactor and temperature is inserted instead of the function $\rho_A(x,t)$. If the thermal insulation of the end wall of the reactor is imperfect, the boundary condition (*4*) must be replaced by the boundary condition of the third kind – Eq. (*15*), hence, the gradient at the outlet will be different from zero.

The above reasoning suggests that if the principally less correct diffusion model (*1*) is adopted, the boundary conditions (*3*) and (*4*) can provide a more realistic description of actual reactors than the adoption of the more correct conditions of continuity of the functions and their gradients at the reactor inlet. This approach is consistent with the conclusions of Deckwer and Mahlman[30], who noticed that eddy diffusion inside a reactor does not cause backward fluctuations of the particle motion.

CONCLUSIONS

The following steps were made in the treatment:

1. The general diffusion equation in three spatial dimensions (Eq. (*6*)) along with the boundary conditions (Eqs. (*10*) and (*11*)) was formulated so as to enable the component mass or heat transport inside a flow system to be described.

2. These equations were compared to the analogous Kolmogorov (Fokker–Planck) diffusion equation for the probability density and to the boundary conditions conventionally used in stochastic process theory (Eq. (*21*)). It was concluded that the probabilistic form of the diffusion equation is only suitable for a class of problems which is narrower than the class of problems that can be solved by using the conventional diffusion equation.

3. The approach described in this paper allows the model of one-dimensional flow reactor to be treated from a rather general point of view, and the Danckwert's boundary conditions[10] to be interpreted in a more appropriate way.

4. It is suggested that the above deficiencies of the diffusion model can be eliminated by using the so-called dynamic model which takes into account the velocities of the moving molecules.

SYMBOLS

a	constant in Eq. (*22*), m s^{-1}
b	constant in Eq. (*22*)
$\boldsymbol{b}$	arbitrary vector
C_1	constant in Eq. (*15*), m^{-1}
C_2	constant in Eq. (*15*), kg m^{-4}
$\boldsymbol{D}$	diffusion tensor, $m^2\ s^{-1}$
D	diffusivity, $m^2\ s^{-1}$
f_v	probability density function for particle velocity, m^{-1} s
$\boldsymbol{G}$	stochastic tensor, m $s^{-1/2}$
L	reactor or mixer lenght, m
$\boldsymbol{n}$	unit vector of external normal at a point of surface S
p	probability density for particle position, m^{-3}
$\boldsymbol{q}$	intensity of flux of component A, kg $m^{-2}\ s^{-1}$
$\boldsymbol{r}$	position vector of points forming surface S, m
r	reaction rate, kg $m^{-3}\ s^{-1}$
S	boundary (surface) of region Ω_R, m^2
t	time, s
$\boldsymbol{V}$	stochastic velocity of particle, m s^{-1}
$\boldsymbol{v}$	velocity of fluid, m s^{-1}
$\boldsymbol{W}$	three dimensional Wiener process, $s^{1/2}$
$\boldsymbol{X}$	position vector of particle position, m
x	spatial coordinate, m
α	constant in Eq. (*23*) characterizing the active force, m s^{-2}
β	constant in Eq. (*23*) characterizing the force of laminar friction, s^{-1}

γ constant in Eq. (*23*) characterizing the force of turbulent friction, s^{-1}
ρ_A concentration of component A, kg m^{-3}
Ω_R region (volume) of space, m^3

Subscripts

e related to outlet opening
i related to inlet opening
n related to external normal direction
0 related to initial condition
T related to turbulent flow
u related to impermeable part of surface

REFERENCES

1. Kudrna V.: Collect. Czech. Chem. Commun. *53*, 1181 (1988).
2. Kudrna V.: Collect. Czech. Chem. Commun. *53*, 1500 (1988).
3. Kudrna V., Turzík D.: Collect. Czech. Chem. Commun. *57*, 1248 (1992).
4. Feller W.: Ann. Math. *55*, 468 (1952).
5. Feller W.: Trans. Amer. Math. Soc. *77*, 1 (1954).
6. Bharucha-Reid A. T.: *Elements of the Theory of Markov Processes and Their Applications*. Nauka, Moscow 1969.
7. Dynkin E. B., Yushkevich A. A.: *Teoremy i zadachi o protsessakh Markova*. Nauka, Moskva 1967.
8. Gardiner C. W.: *Handbook of Stochastic Methods for Physics, Chemistry and Natural Sciences*. Springer, Berlin 1985.
9. Friedman A.: *Partial Differential Equations of Parabolic Type*. Prentice-Hall, Englewood Cliffs 1964.
10. Danckwerts P. V.: Chem. Eng. Sci. *2*, 1 (1953).
11. Wen C. W., Fan L. T.: *Models for Flow Systems and Chemical Reactors*. Dekker, New York 1975.
12. Nauman E. B., Buffham B. A.: *Mixing in Continuous Flow Systems*. Wiley, New York 1983.
13. Naumann E. B.: Chem. Eng. Sci. *36*, 957 (1981).
14. Brenner H.: Chem. Eng. Sci. *17*, 229 (1962).
15. Bischoff K. B.: Chem. Eng. Sci. *16*, 131 (1961).
16. Wehner J. F., Wilhelm R. H.: Chem. Eng. Sci. *6*, 89 (1955).
17. Ladyzhenskaya O. A., Solonnikov V. A., Uraltseva N. N.: *Lineinye i kvazilineinye uravnenia parabolicheskogo tipa*. Nauka, Moscow 1967.
18. Parulekar S. J., Ramkrishna D.: Chem Eng. Sci. *39*, 1571 (1984).
19. Parulekar S. J., Ramkrishna D.: Chem Eng. Sci. *39*, 1581 (1984).
20. Pearson J. R. A.: Chem. Eng. Sci. *10*, 281 (1959).
21. Kershenbaum L., Perkins J. D.: Chem. Eng. Sci. *29*, 624 (1974).
22. Choi C. Y., Perlmutter D. D.: Chem. Eng. Sci. *31*, 250 (1976).
23. Dilman V. V., Kronberg A. E.: Teor. Osn. Khim. Tekhnol. *17*, 614 (1983).
24. Dilman V. V., Kronberg A. E.: Khim. Prom-st. (Moscow) *1983* (8), 464.
25. Dilman V. V.: Teor. Osn. Khim. Tekhnol. *21*, 66 (1987).
26. Madelung E.: *Die mathematischen Hilfsmittel des Physikers*. Springer, Berlin 1957.
27. Kudrna V.: Collect. Czech. Chem. Commun. *44*, 1094 (1979).

28. Kudrna V., Hasal P., Vejmola L.: Collect. Czech. Chem. Commun., submitted.
29. Rippin D. W. T.: Ind. Eng. Chem., Fundam. *6*, 488 (1967).
30. Deckwer W. D., Mahlman E. A.: Chem. Eng. Sci. *31*, 1221 (1976).

Translation revised by P. Adamek.