

**CERTAIN PROBLEMS WITH THE APPLICATION  
OF STOCHASTIC DIFFUSION PROCESSES  
FOR THE DESCRIPTION OF CHEMICAL ENGINEERING PHENOMENA.  
STOCHASTIC MODEL OF ISOTHERMAL CONTINUOUS FLOW  
CHEMICAL REACTOR**

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A model of an isothermal one-dimensional continuous flow chemical reactor operating at the steady state was derived using a stochastic description of motion of the reacting molecules. The model enables evaluation of the conversion of the reacting components. At the limiting parameter values the model yields results identical to those of the simplified models conventionally used in chemical reactor engineering. The model also enables the applicability of Danckwerts' boundary conditions to be assessed from a more general point of view.

In our previous paper<sup>1</sup> a stochastic model of one-dimensional continuous closed mixer (cf. Fig. 1) was set up to demonstrate the applicability of the general approach<sup>2</sup> to the formulation of boundary conditions for flow-through mixers and chemical reactors. An incompressible liquid flowing through the mixer and carrying molecules of a non-reacting component A was considered. The molecules were supposed to move under the influence of deterministic as well as stochastic forces. These forces were assumed to be linear functions of velocity of the molecule. The equation of molecular motion then has the form of a stochastic differential equation (cf. Eqs (1) and (2) in ref.<sup>1</sup>). The inlet of the mixer was considered to be a reflecting boundary<sup>3</sup>, the outlet was considered to be an elastic boundary<sup>3</sup>. The ratio of the probability of reverberation of a molecule to that of the molecule escaping from the mixer was assumed to be directly proportional to the instantaneous molecule velocity (cf. Eq. (17) in ref.<sup>1</sup>). Such boundary conditions enabled a quantitative description of the circulation of the liquid and the component A within the mixer to be formulated.

A diffusion equation (Eq. (7) in ref.<sup>1</sup>) corresponding to the stochastic differential equations (1) and (2) in ref.<sup>1</sup> was set up and solved for the joint probability density of molecule position and velocity under the assumption that forces acting on the mole-

cules are negligible in the mixer except in the space close to its inlet and outlet. In this way, two parameter models for the component concentration profile along the mixer (cf. Eq. (33) in ref.<sup>1</sup>) and for the liquid residence time distribution (cf. Eq. (34) in ref.<sup>1</sup>) were derived.

In the present paper, this approach is extended to systems with reacting components, i.e. to continuous flow chemical reactors.

## THEORETICAL

The assumptions reviewed in the preceding paragraph will be completed here with the following assumptions:

1. Component A entering the reactor via its inlet stream is consumed in a chemical reaction occurring inside the system:



2. The process is isothermal and steady-state.

3. The concentration of the reacting component A is low enough not to influence the flow pattern within the system.

4. Molecules of component A are carried by the circulating liquid and reverberate at the two system boundaries. They can escape from the system with a probability  $p$  before they are consumed by the chemical reaction.

The liquid flow and motion of molecules of component A are assumed to take place in stream tubes occupying the whole reactor volume. The total number of stream tubes is  $2n + 1$ , where  $n$  is the number of molecule reverberations at the reactor outlet wall. In  $n + 1$  stream tubes the liquid moves in the positive direction of the longitudinal axis of the mixer, whereas in  $n$  stream tubes the liquid moves in the opposite direction. The concept of stream tubes enables the total reactor volume to be divided into parts with

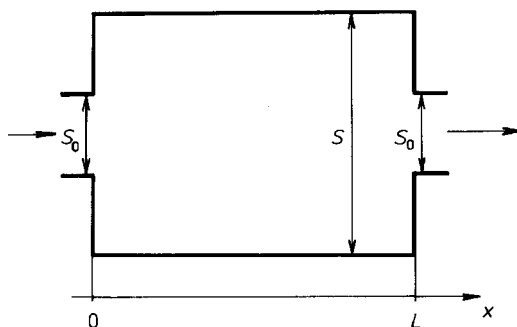


FIG. 1

Layout of a continuous flow closed chemical reactor

different directions of liquid motion and liquid circulation to be introduced into the model. We will refer to the stream tube containing liquid which entered the reactor and has not yet been reverberated at the reactor outlet as the primary stream tube. A fraction of both the liquid and molecules of component A can leave the reactor during each reverberation at the outlet. The remaining part swaps to another stream tube where it moves in the opposite direction. Thus, the cross-section of the stream tubes decreases with increasing liquid residence time.

Mass exchange between the stream tubes (e.g. by molecular diffusion) is assumed to be negligible. We will refer to the concentration  $c$  of component A within a single stream tube as the local concentration. The kinetic parameter of the reaction rate equation for a particular stream tube can depend on the local concentrations in other stream tubes. A molecule of component A thus can react with molecules of A in other stream tubes. The diffusion (mass balance) equations for component A in an isothermal steady-state reaction then is

$$v \frac{dc_n^+}{dx} = \Psi(\mathbf{c}) c_n^+, \quad (n = 0, 1, 2, \dots)$$

$$-v \frac{dc_n^-}{dx} = \Psi(\mathbf{c}) c_n^-, \quad (n = 1, 2, 3, \dots), \quad (I)$$

where  $c_n^+$  is the concentration of A within a stream tube in which the liquid carries the component A with a velocity  $v$  towards the reactor outlet after the  $n$ -th reverberation at the outlet wall (cf. Eqs (18) in ref.<sup>1</sup>). The symbol  $c_n^-$  denotes the concentration of component A during its motion from the outlet to the inlet wall. The proportionality factor (kinetic "constant")  $\Psi$  does not depend on temperature but can be a function of the vector of local concentrations  $\mathbf{c} = [c_0^+, c_1^+, \dots, c_n^+, c_1^-, c_2^-, \dots, c_n^-]$ . The kinetic term in Eqs (I) is formally written for a first order chemical reaction. However, since parameter  $\Psi(\mathbf{c})$  depends on the local concentrations in all stream tubes, Eqs (I) hold for general order reactions. The concentration of component A at position  $x$  can be defined as the average of local concentrations over the reactor cross-section perpendicular to its longitudinal axis weighed by the probability of a molecule being still trapped within the reactor after the  $n$ -th reverberation:

$$\rho_A(x) = \left( \sum_{n=0}^{\infty} c_n^+(x) q^n + \sum_{n=1}^{\infty} c_n^-(x) q^n \right) g, \quad (q = 1 - p). \quad (2)$$

The quantity  $g$ ,

$$g = \frac{1 - q}{1 + q}, \quad (3)$$

is the normalization factor, as can be demonstrated by considering the non-reacting component A when all local concentrations are equal to the inlet concentration  $\rho_{A0}$ . The probability  $q$  is a measure of the stream tube cross-section contraction during each reverberation. With regard to Eq. (17) in ref.<sup>1</sup>,  $q$  is a function of the liquid velocity  $v$ :

$$\frac{q}{p} = \frac{v}{w}, \quad w = \frac{2\dot{V}}{S - S_0}, \quad (4)$$

where constant  $w$  depends on the liquid volumetric flow rate through the reactor  $\dot{V}$  and on the system configuration (cf. Fig. 1). If the cross-section  $S$  of the reactor interior equals the cross-sections of the inlet and outlet openings, parameter  $q$  is zero, which is the case of the so-called open reactor<sup>1</sup>.

By summing Eqs (1) multiplied by the term  $q^n$  and the normalization factor  $g$  we obtain

$$v \frac{dm_A(x)}{dx} = \Psi(\mathbf{c}) \rho_A(x) = \Phi(\rho_A). \quad (5)$$

The function  $m_A(x)$  can be regarded as the differential concentration of component A between the stream tubes with opposite flow directions:

$$m_A(x) = \left( \sum_{n=0}^{\infty} c_n^+(x) q^n - \sum_{n=1}^{\infty} c_n^-(x) q^n \right) g. \quad (6)$$

The function  $\Phi(\rho_A)$  in Eq. (5) denotes the reaction rate. The coefficient  $\Psi(\mathbf{c})$  in Eqs (1) has the form (cf. Eq. (5))

$$\Psi(\mathbf{c}) = \frac{\Phi(\rho_A)}{\rho_A}. \quad (7)$$

This relation defines the proportionality parameter  $\Psi(\mathbf{c})$  as the kinetic parameter of the chemical reaction. The actual form of Eq. (7) is determined by results of kinetic experiments.

Equation (5) involves two functions of the position  $x$ , therefore it cannot be solved directly. However, the function  $m_A(x)$  can be expressed by means of  $\rho_A(x)$ , and so the result of the summing Eqs (1) is given by the ordinary differential equation

$$v \frac{d\rho_A(x)}{dx} = \Phi[\rho_A(x)] \frac{[\rho_A^2(x) - \rho_{Ak}^2(1 - g^2)]^{1/2}}{\rho_A(x)}, \quad (8)$$

where  $\rho_{Ak} \equiv \rho_A(L)$  is the component A concentration at the reactor outlet (cf. Eq. (A9), see Appendix). The boundary condition  $\lim_{x \rightarrow 0} \rho_A(x) = \rho_{A0}$  is only satisfied if  $q = 0$ , i.e. in an open reactor (cf. Eq. (A14)). This implies that the average concentration of component A at the reactor inlet is lower than the concentration within the inlet stream due to the liquid circulation when the liquid with a low concentration of A (component A is consumed by chemical reaction) returns from the reactor outlet back to the inlet. The concentration of component A within the primary stream tube at the reactor inlet, however, equals the inlet concentration  $\rho_{A0}$  for any value of  $q$  (cf. the first of Eqs (A3)).

Equation (8) can only be solved by iterations because its right-hand side involves the outlet concentration  $\rho_{Ak}$ . However, it is possible to evaluate this concentration making use of the following integral:

$$\rho_{A0} \int_1^{\rho_{Ak}/\rho_{A0}} \frac{g \, da}{\Phi[(ag\rho_{A0})^2 + (1-g^2)\rho_{Ak}]^{1/2}} = \frac{L}{v} \quad (9)$$

(see Appendix). Obviously, the quantity  $\rho_{Ak}$  can be evaluated by numerical methods only. The numerical procedure, however, is quite simple. After solving Eq. (9) for  $\rho_{Ak}$ , the differential equation (8) can also be easily solved, yielding the concentration profile of component A along the reactor. In general, this concentration is a function of liquid velocity  $v$ . Velocity randomization<sup>4</sup> leads to the average concentration:

$$\bar{\rho}_A(x) = \int_0^{\infty} \rho_A(x,v) f_v(v) \, dv \quad (10)$$

This equation also holds for the outlet concentration of component A, which is the quantity that is usually sought. The probability density function for the velocity distribution is given by the relation (cf. Eq. (9) in ref.<sup>1</sup>)

$$f_v(v) = \frac{(e/v)^{b+1}}{e\Gamma(b)} \exp\left(-\frac{e}{v}\right), \quad (11)$$

where parameters  $e$  and  $b$  depend on forces acting on the molecule<sup>1</sup> (cf. Eq. (9) in ref.<sup>1</sup>).

The above procedure enables us to compute the conversion of the reacting component in an isothermal flow reactor at the steady state.

The first derivative of the concentration of component A at the outlet ( $x = L$ ) with respect to the longitudinal coordinate is

$$\left. \frac{d\rho_A(x)}{dx} \right|_{x=L} \equiv \delta_L = \Phi(\rho_{Ak}) \frac{g}{v} \quad (12)$$

In analogy with Eq. (10) a value of this derivative averaged with respect to the velocity distribution can be evaluated as

$$\bar{\delta}_L = \int_0^{\infty} \delta_L(v) f_v(v) dv . \quad (13)$$

Unlike the commonly adopted (but somewhat speculative) Danckwerts' boundary condition for reactor outlet<sup>5</sup>, this averaged derivative will not in general be zero.

By introducing the following dimensionless variables for the liquid velocity, the longitudinal coordinate, the concentration of component A, the reaction rate, and the spatial concentration derivative,

$$\begin{aligned} v^* &= (v\varphi)/e = (v\varphi)/(\omega b\Omega) , & \varphi &= b(1 + 2\Omega) , \\ x^* &= x/L , \\ \rho_A^* &= \rho_A/\rho_{A0} , \\ \Phi^*(\rho_A^*) &= \bar{\tau}(\Phi[\rho_A^*\rho_{A0}])/\rho_{A0} , \\ \delta_1^* &= (\delta_L L)/\rho_{A0} , \end{aligned} \quad (14)$$

the relations derived in the previous paragraphs can be transformed into dimensionless forms. In Eqs (14),  $\Omega$  is the intensity of liquid circulation within the reactor and  $\bar{\tau}$  is the mean liquid residence time<sup>1</sup>.

The probability density of the dimensionless velocity of molecules is

$$f_{v^*}(v^*) = f_v\left(\frac{v^*e}{\varphi}\right) \frac{e}{\varphi} = \exp\left(-\frac{\varphi}{v^*}\right) \frac{(\varphi/v^*)^{b+1}}{\varphi\Gamma(b)} . \quad (15)$$

The probability  $q$  of reverberation of a molecule at the reactor outlet can be expressed as a function of the dimensionless velocity  $v^*$  and the circulation intensity  $\Omega$ :

$$q = \frac{\Omega v^*}{\Omega v^* + 2\Omega + 1} , \quad (16)$$

and parameter  $g$  is defined as

$$g = \frac{2\Omega + 1}{2\Omega v^* + 2\Omega + 1} . \quad (17)$$

Using Eqs (14) – (17), the dimensionless forms of Eqs (8), (9), (10), (12) and (13) can be easily derived. For the sake of brevity, this transformation is not shown here.

The conversion of component A at the reactor outlet is obviously

$$\xi_A = 1 - \bar{\rho}_{Ak}^* \quad (18)$$

## RESULTS AND DISCUSSION

In our previous paper<sup>1</sup>, the above approach to the modelling of flow systems was discussed from the point of view of liquid residence time distribution in a continuous flow mixer. The physical meaning of parameters  $\Omega$  and  $b$  was analyzed along with the model behavior at the limiting parameter values.

Now, the behavior of the model of an isothermal continuous flow chemical reactor derived in the previous section will be analyzed and the results of the conversion evaluation for the first order

$$\Phi^* = -k\rho_A^* \quad (19)$$

and the second order

$$\Phi^* = -k\rho_A^{*2} \quad (20)$$

chemical reaction (cf. comment post Eq. (1)) will be presented (see Figs 2 and 3). The coefficient  $k$  in Eqs (19) and (20) is the kinetic constant for the dimensionless reaction rate equation ( $k = k_v \bar{t} / \rho_A^{v-1}$ ), where  $k_v$  is the dimensional kinetic constant and  $v$  is the order of reaction.

First, the behavior of the model will be analyzed at particular parameter values:

1.  $\Omega \rightarrow 0$ : It has been proved<sup>1</sup> that this holds in an open reactor. The dimensionless form of Eq. (9) simplifies to

$$\int_1^{\rho_{Ak}^*} \frac{da}{\Phi^*(a)} = \frac{1}{v^*} \quad (21)$$

This case was discussed in detail earlier by Kudrna<sup>4</sup>. Only two particular cases are dealt with here.

*Ia.*  $\Omega \rightarrow 0$  and  $b \rightarrow \infty$ : This combination of parameter values corresponds to the liquid plug-flow inside the reactor. The conversion of component A in a second order chemical reaction for this case is shown as points A and B in Fig. 2.

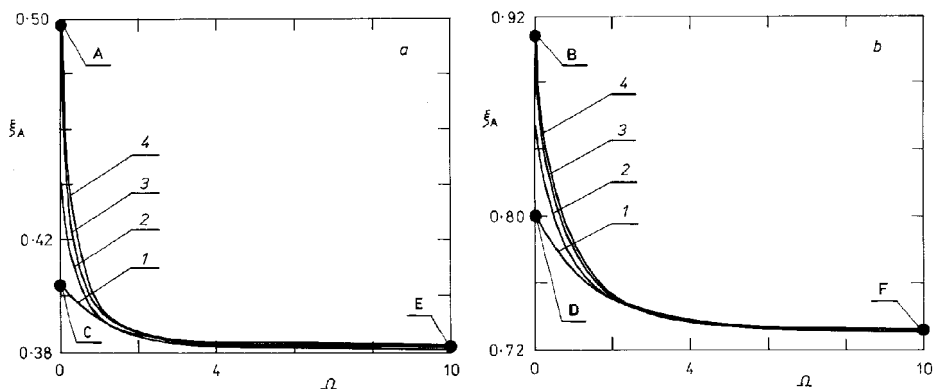


FIG. 2

Conversion of reacting component as a function of parameter  $b$  for a second order chemical reaction  $\Phi^* = -k\rho_A^{*2}$ ;  $a k = 1$ ,  $b k = 10$ ; 1  $b = 1$ , 2  $b = 2$ , 3  $b = 4$ , 4  $b = 50$ . Limiting conversion values: A plug-flow (case *Ia*),  $\xi_A = 0.5$ ; B plug-flow (case *Ia*),  $\xi_A = 0.909$ ; C ideal macromixing (case *Ib*),  $\xi_A = 0.404$ ; D ideal macromixing (case *Ib*),  $\xi_A = 0.799$ ; E ideal micromixing (case 2),  $\xi_A = 0.382$ ; F ideal micromixing (case 2),  $\xi_A = 0.730$

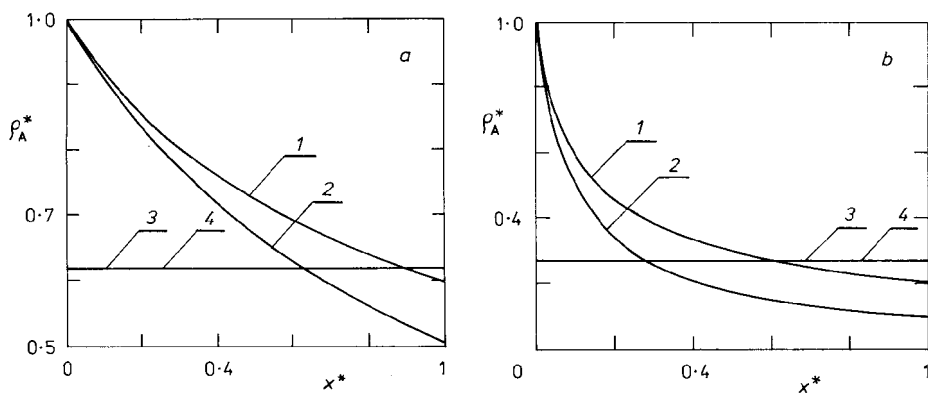


FIG. 3

Concentration profiles of the reacting component along the reactor for a second order chemical reaction  $\Phi^* = -k\rho_A^{*2}$ ;  $a k = 1$ ,  $b k = 10$ ; 1  $b = 1$ ,  $\Omega = 0$ ; 2  $b = 30$ ,  $\Omega = 0$ ; 3  $b = 1$ ,  $\Omega = 30$ ; 4  $b = 30$ ,  $\Omega = 30$



*1b.*  $\Omega \rightarrow 0$  and  $b \rightarrow 1$ : This combination of parameter values describes an ideally stirred continuous flow reactor with liquid macromixing. The conversion of component A for a second order chemical reaction is indicated by points C and D in Fig. 2.

*2.*  $\Omega \rightarrow \infty$ : This case describes an ideally stirred continuous flow reactor with liquid micromixing. Integration of Eq. (9) yields the relation

$$\rho_{Ak}^* - 1 = \Phi^*(\rho_{Ak}^*) , \quad (22)$$

i.e. the dimensionless form of mass balance of the reactor. The conversion of component A in a second order chemical reaction is indicated by points E and F in Fig. 2.

Equation (8) enables the concentration profile of the reacting component along the reactor to be evaluated. At a zero circulation intensity ( $\Omega \rightarrow 0$ ) and at high  $b$  values ( $b = 30$ ) the concentration profile is nearly identical with the profile inside a reactor with the plug-flow (cf. Fig. 3, curves 2). In the ideally stirred reactor with macromixing ( $\Omega \rightarrow 0$ ,  $b = 1$ ) the dimensionless concentration also varies markedly along the reactor (cf. Fig. 3, curves 1). The concentration of component A at the reactor inlet ( $x^* = 0$ ) is equal to the inlet concentration in both cases. At relatively high circulation intensities ( $\Omega = 30$ ), on the other hand, the mixing regime inside the reactor approaches micromixing and the concentration of the reacting component varies very little with position and is nearly independent of the value of  $b$  (cf. Fig. 3, curves 3 and 4). A step change in concentration occurs at the reactor inlet due to the lower component concentration in the recirculating liquid stream (cf. also ref.<sup>2</sup>).

The boundary conditions based on the idea of reverberation of the reacting molecules at the reactor outlet enabled us to express the longitudinal derivative of the reacting component concentration at the outlet (see Eq. (12)). The dimensionless value of this derivative converges to  $\Phi^*(\rho_{Ak}^*)$  when the flow regime approaches the plug-flow, because the parameter  $g$  (see Eqs (3) and (17)) converges to unity, i.e. to the value predicted by differential mass balance for the tube reactor with plug-flow. As the flow regime approaches the ideally stirred reactor with micromixing, parameter  $g$  converges to zero and the concentration derivative at the outlet converges quickly to zero as well. The two cases are shown in Fig. 4 for the second order chemical reaction.

In the previous papers<sup>1,2</sup> it was emphasized that diffusion models of the dynamical type, i.e. models involving inherently distribution of velocities of the reacting molecules, are more general than the conventional diffusion models of the kinematic type describing the position vectors of molecules only and supposing implicitly infinitely large molecule velocities at any moment. The model presented in this and the previous papers<sup>1</sup> involves the distribution of molecule velocities. In its general form, however, the model is too complex. The simplifications adopted in the papers (reduction of the spatial molecule motion to a single dimension and assumption of local action of mecha-

nical forces in the vicinity of the reactor boundaries only) enable the formulas to be easily solved numerically, although at the expense of generality and accuracy. So, it is of interest to compare the presented model with the classical diffusion model

$$\frac{1}{Pe} \frac{d^2 \rho_A^*}{dx^{*2}} - \frac{d\rho_A^*}{dx^*} + \Phi^*(\rho_A^*) = 0, \quad Pe = \frac{\bar{v}L}{D}, \quad (23)$$

with the boundary conditions proposed by Danckwerts<sup>5</sup>, viz.

$$\lim_{x^* \rightarrow 0^+} \left[ \rho_A^*(x^*) - \frac{1}{Pe} \frac{d\rho_A^*(x^*)}{dx^*} \right] = 1, \quad (24)$$

$$\lim_{x^* \rightarrow 1^-} \frac{d\rho_A^*(x^*)}{dx^*} = 0.$$

Although both models predict a concentration jump at the reactor inlet, only the dynamical model explains its cause. The circulation of the reacting component is responsible for a decrease in its concentration within the region close to the reactor inlet, when the component concentration equals the inlet value only within the primary stream tube (cf. the first boundary condition for Eq. (A3)).

Unlike Danckwerts' model, the dynamical model eliminates the discontinuity of the concentration derivative at the reactor outlet (cf. Eqs (24)) when the liquid flow regime inside the reactor approaches the plug-flow. At an increased circulation intensity, i.e.,

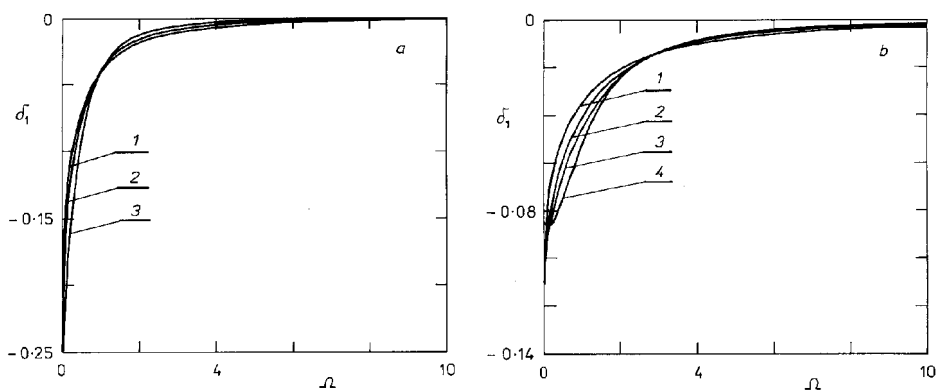


FIG. 4

Spatial derivative of concentration of the reacting component at the reactor outlet as a function of model parameters for a second order chemical reaction  $\Phi^* = -k\rho_A^{*2}$ ;  $a k = 1$ ,  $1 b = 1$ ,  $2 b = 2$ ,  $3 b = 50$ ;  $b k = 10$ ,  $1 b = 1$ ,  $2 b = 2$ ,  $3 b = 4$ ,  $4 b = 50$

at a low Peclet number, the concentration derivative value is very low, which proves the applicability of the speculative Danckwerts' boundary condition in computations requiring routine (engineering) accuracy.

In our opinion there is no point in discussing the correctness or incorrectness of Danckwerts' boundary condition (see e.g. ref.<sup>6</sup>) if the conventional diffusion models themselves fail to describe the physical reality with a sufficient precision, and may even yield results which are in contradiction to logical reasoning<sup>7</sup>.

The relations for the variance of the dimensionless residence time (a quantity which can be easily derived from experimental data) were used to compare the two models quantitatively. Levenspiel and Smith<sup>8</sup> derived a relation for the variance of the residence time for Danckwerts' model (DM)

$$\sigma_{DM}^2 = \frac{2}{Pe} \left( 1 - \frac{\exp(-Pe)}{Pe} \right). \quad (25)$$

Using Eq. (35) in ref.<sup>1</sup>, a relation for the residence time variance in the dynamical stochastic model (DSM) was derived assuming that the Peclet number is conversely proportional to the intensity of liquid circulation:

$$\sigma_{DSM}^2 = 1 + \frac{1/b - 1}{(1 + h/Pe)^2}. \quad (26)$$

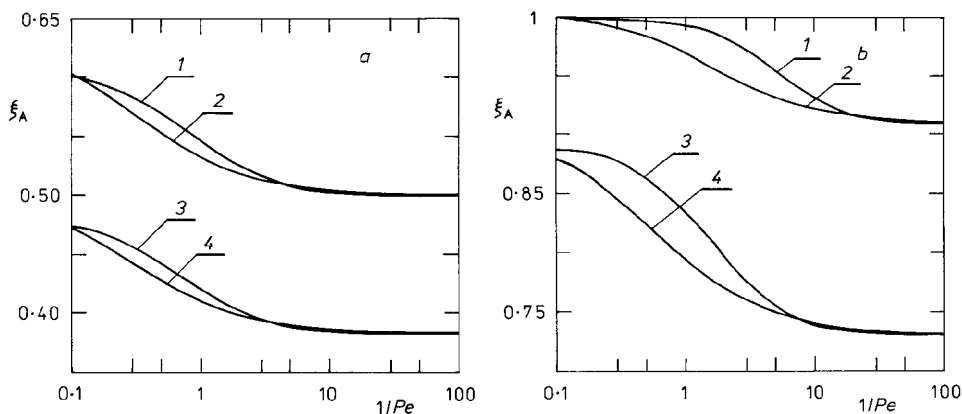


FIG. 5

Conversion of the reacting component at the reactor outlet as a function of the Peclet number  $a$   $k = 1$ ;  $b$   $k = 10$ ; a first order reaction:  $\Phi^* = -k \rho_A^*$ , 1 dynamical stochastic model (DSM), 2 Danckwerts' model (DM); a second order reaction:  $\Phi^* = -k \rho_A^{*2}$ , 3 dynamical stochastic model (DSM), 4 Danckwerts' model (DM)

By putting Eqs (25) and (26) equal, the values of  $b$  and  $h$  in Eq. (26) corresponding to  $0 < 1/Pe < 10$  were estimated using a nonlinear regression method<sup>9</sup>. The procedure gave  $b = 8.99$  and  $h = 0.736$ . These values were used for a mutual conversion of the DM and DSM parameters in simulating computations. The conversion  $\xi_A$  was evaluated for irreversible chemical reactions of the first and second orders at various  $Pe$  values for the two models (Fig. 5). The results indicate that the difference between the two models is relatively small at high  $Pe$  values, i.e. at a flow regime approaching closely the plug-flow. The dynamical model yields a somewhat higher conversion than Danckwerts' model. At low  $Pe$  values, i.e. at a flow regime approaching ideal stirring, the difference in conversion between the two models is negligible.

If a routine precision is sufficient, the results of the two models can be considered equivalent. Discrimination between the models can only be made based on precise experiments enabling detection of very low differences in conversion.

## CONCLUSIONS

1. The proposed dynamical model of an isothermal continuous flow chemical reactor enables the conversion of a reacting component at the steady state to be evaluated.

2. The dynamical model involving the distribution of velocities of the reacting molecules can be regarded as a refinement of the conventional diffusion model, which is widely adopted in chemical engineering. The refinement is more important from the theoretical point of view (the model can solve some problems where the conventional diffusion model applied to the description of real continuous reactors of mixers fails) than from the point of view of the conversion evaluation for a particular reactor and particular reaction kinetics.

3. The dynamical model presented in this paper suitably illustrates the general conclusions made previously<sup>2</sup>.

## APPENDIX

### *Evaluation of Concentration of the Reacting Component in an Isothermal Continuous Flow Reactor at the Steady State*

By means of the relation (5), Eq. (1) can be rearranged to

$$v \frac{d \ln (c_n^+)}{dx} = \frac{\Phi(\rho_A)}{\rho_A}, \quad (n = 0, 1, 2, \dots),$$

$$-v \frac{d \ln (c_n^-)}{dx} = \frac{\Phi(\rho_A)}{\rho_A}, \quad (n = 1, 2, \dots). \quad (A1)$$

The right-hand sides of Eqs (A1) are mutually equal. Therefore, any concentration can be expressed as a function of any of the remaining concentrations. Thus the individual concentrations in Eqs (2) and (6) expressed as functions of the concentration  $c_0^+$  within the primary stream tube have the form

$$c_n^+(x) = K_n^+ c_0^+(x) \quad , \quad c_n^-(x) = K_n^- c_0^+(x) \quad , \quad (A2)$$

where  $K_n^\pm$  are integration constants which can be determined using the boundary conditions of Eqs (A1)

$$\lim_{x \rightarrow 0^+} c_0^+(x) = \rho_{A0} \quad ; \quad \lim_{x \rightarrow 0^+} c_n^+(x) = \lim_{x \rightarrow 0^+} c_n^-(x) \quad ;$$

$$\lim_{x \rightarrow L^-} c_n^-(x) = \lim_{x \rightarrow L^-} c_{n-1}^+(x) \quad ; \quad (n = 1, 2, \dots) \quad . \quad (A3)$$

It follows from Eqs (A1) that all logarithmic decrements of the solutions are identical. Therefore, the following relations hold:

$$K_n^+ = \left[ \frac{c_0^+(0)}{c_0^+(L)} \right]^{2n} \quad ; \quad K_n^- = \left[ \frac{c_0^+(L)}{c_0^+(0)} \right]^{2n} c_0^+(0)^2 \quad , \quad (n = 1, 2, \dots) \quad . \quad (A4)$$

Knowing the ratio  $c_0^+(0)/c_0^+(L)$ , all integration constants  $K_n^\pm$  can be easily found. Therefore, after introducing a new variable

$$s \equiv q \left[ \frac{c_0^+(L)}{c_0^+(0)} \right]^2 \quad (A5)$$

and substituting from Eqs (A2), (A4) and (A5) into Eq. (2), the following relation is obtained:

$$\rho_A(x) = \rho_{A0} g \left[ c_0^{*+} \sum_{n=0}^{\infty} s^n + \frac{1}{c_0^{*+}} \sum_{n=1}^{\infty} s^n \right] = \frac{\rho_{A0} g (c_0^{*+} + s/c_0^{*+})}{1-s} \quad , \quad (A6)$$

where  $g$  ( $s < g < 1$ ) is defined by Eq. (3) and

$$c_0^{*+}(x) = \frac{c_0^+(x)}{\rho_{A0}} \quad . \quad (A7)$$

Similarly, Eq. (6) transforms to

$$m_A(x) = \frac{\rho_{A0} g \left[ c_0^{*+}(x) - \frac{s}{c_0^{*+}(x)} \right]}{1 - s} . \quad (A8)$$

Now, the terms involving local concentrations, i.e.  $c_0^{*+}(x)$  and  $s$ , will be eliminated. It follows from Eqs (A7), (A5) and the first boundary condition (A3) that  $c_0^{*+}(L) = (s/g)^{1/2}$ , so that the following relation is obtained by substituting in Eq. (A6) at  $x = L$ :

$$\rho_{Ak} = \rho_A(L) = \rho_{A0} \frac{1 - q}{1 - s} (s/q)^{1/2} . \quad (A9)$$

Subtracting the square powers of Eqs (A6) and (A8) we obtain the relation

$$\rho_A^2(x) - m_A^2(x) = \frac{4\rho_{A0}^2 g^2 s}{(1 - s)^2} , \quad (A10)$$

which (with regard to Eqs (A9) and (3)) simplifies to

$$\rho_A^2(x) - m_A^2(x) = \rho_{Ak}^2 (1 - g^2) . \quad (A11)$$

The right-hand side of this equation is independent of  $x$ , so that the following relation holds:

$$\frac{dm_A}{dx} = \frac{d\rho_A}{dx} \frac{\rho_A}{m_A} = \frac{d\rho_A}{dx} \frac{\rho_A}{[\rho_A^2 - \rho_{Ak}^2(1 - g^2)]^{1/2}} . \quad (A12)$$

The differential equation (8) is obtained by substitution from Eq. (A12) into Eq. (5). The initial value of the differential concentration is independent of the local concentrations, because Eqs (A7) and (A8) give

$$\lim_{x \rightarrow 0^+} c_0^{*+}(x) = 1 , \quad \lim_{x \rightarrow 0^+} m_A(x) = \rho_{A0} g . \quad (A13)$$

The initial value of the (averaged) concentration of component A can be derived (after some rearrangements) from Eqs (A11) and (A13) as

$$\lim_{x \rightarrow 0^+} \rho_A(x) = \rho_{A0} [g^2(1 - \rho_{Ak}^{*2}) + \rho_{Ak}^{*2}]^{1/2} . \quad (A14)$$

This equation, along with the fact that  $\rho_{Ak}/\rho_{A0} = \rho_{Ak}^* < 1$ , leads to the inequality  $\rho_A(0) \leq \rho_{A0}$ ; the equality is only possible when  $q = 0 \Rightarrow g = 1$ , i.e. in the open reactor.

For simplification, a new function  $a = a(x)$  will be introduced as

$$a(x) = \frac{m_A(x)}{\rho_{A0} g} . \quad (A15)$$

Substitution from Eqs (A10) and (A15) into Eq. (5) and separation of variables gives the final differential equation

$$\rho_{A0} \frac{g da}{\Phi[(\rho_{A0} g a)^2 + (1 - g^2) \rho_{Ak}^{*2}]^{1/2}} = \frac{dx}{v} . \quad (A16)$$

Using Eq. (A13) at  $x \rightarrow 0+$  together with Eqs (A11) and (A15) at  $x \rightarrow L-$ , the integration limits for the integral in Eq. (9) can be found in the form

$$\lim_{x \rightarrow 0+} a(x) = 1 , \quad \lim_{x \rightarrow L-} a(x) = \frac{\rho_{Ak}}{\rho_{A0}} . \quad (A17)$$

## SYMBOLS

(Numbers in brackets refer to equations with the first occurrence of the symbols)

$a$	integration variable (9)
$b$	parameter of gamma-distribution (11)
$c$	local component concentration (1), $\text{kg m}^{-3}$
$\mathbf{c}$	vector of local concentrations (1), $\text{kg m}^{-3}$
$D$	dispersion coefficient (23), $\text{m}^2 \text{s}^{-1}$
$e$	constant in Eq. (11), $\text{m s}^{-1}$
$f_v$	probability density function for velocity (11), $\text{m}^{-1} \text{s}$
$g$	parameter defined by Eq. (9)
$h$	proportionality factor (26)
$k$	kinetic constant of dimensionless reaction rate
$K$	integration constant (A2)
$L$	length of reactor (9), m
$m$	differential concentration (5), $\text{kg m}^{-3}$
$n$	number of stream tubes, summation index (1)
$Pe$	Peclet number $Pe = (\bar{v}L)/D$ (23)
$p$	probability of particle escape (2)
$q$	probability of particle reverberation $q = 1 - p$ (2)
$S$	reactor cross-section area, m
$S_0$	reactor inlet and outlet cross-section areas, m
$s$	parameter defined by Eq. (A5)
$\bar{t}$	mean residence time (14), s

$\dot{V}$	volumetric flow rate (4), $\text{m}^3 \text{s}^{-1}$
$v$	velocity of liquid (1), $\text{m s}^{-1}$
$w$	constant in Eq. (4), $\text{m s}^{-1}$
$x$	spatial coordinate (1), m
$\Gamma$	gamma function (11)
$\delta_1$	spatial derivative of dimensionless concentration at reactor outlet (14)
$\xi$	conversion (18)
$\rho$	component concentration (2), $\text{kg m}^{-3}$
$\sigma^2$	variance of dimensionless residence time (25)
$\Phi$	reaction rate (5), $\text{kg m}^{-3} \text{s}^{-1}$
$\Psi$	kinetic parameter (1), $\text{s}^{-1}$
$\varphi$	dimensionless parameter (14)
$\Omega$	circulation intensity (14)

### Subscripts and Superscripts

A	refers to component A
$k$	refers to reactor outlet
$n$	index of stream tube, summation index
0	inlet value
DM	refers to Danckwerts' model
DSM	refers to the dynamical stochastic model
$\pm$	refers to the positive/negative direction of motion
$\bar{u}$	cross-section average of quantity $u$
$u^*$	dimensionless form of variable $u$

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