International Journal of Engineering & Technology, 7 (4.28) (2018) 635 -647

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Stochastic Model of Diffusion Mass Transfer with Sources or Runoffs of Diffusing Substance

Valentin v. Shevelev*

Doctor of Physico-mathematical Sciences, Full Professor, Professor at the Department of Further and Applied Mathematics at MIREA – Russian Technological University, prosp. Vernadskogo 78, Moscow, 119454 Russia;
Professor at the Department of Mathematics at the National University of Science and Technology MISiS, Leninskii prosp. 4, Moscow, 119049 Russia
**E-mail: valeshevelev@yandex.ru*

Abstract

As a rule, the prediction of results of engineering procedures related to the diffusion of an infused component into the treated material confines to solving boundary problems for the diffusion equation defining the change in the average concentration of the infused component. That said, the stochastic component of diffusion mass transfer determined by stochastic boundary conditions and fluctuations in the concentration of diffusing substance in the transfer region is not taken into account, which may significantly affect the prediction of the engineering procedure results. As a consequence, the 1D stochastic model of diffusion mass transfer is developed for the transfer region with third-order stochastic boundary conditions source or runoffs of diffusing substance. The elaborated approach allows one to derive the equation for the probability density of the distribution of the vector characterizing the concentration distribution of diffusing substance in the transfer region against the discrete set of its physically infinitesimal partition volumes in which the local quasi-equilibrium shows. The equation for the multidimensional probability of the concentration distribution of diffusing substance in the transfer region is used to derive the system of equations and formulate the boundary conditions for the unary function of the concentration distribution of diffusing substance, and also define the physical parameters included in the system of equations. The equation for the unary function of the concentration distribution of diffusing substance is used to derive the discretized equations for the core concentration moments basic for deriving the continuant equations for the average concentration and dispersion of diffusing substance. The boundary problems are formulated for the average concentration and dispersion of diffusing substance in case of sources and runoffs of the same type. The approach to finding the parameters of physical infinitesimal volume is formulated.

***Key words**: diffusion, runoff, substance, stochasticity, dispersion*

1.Introduction

Technologies of designing materials with tailor-made properties are usually implemented through the targeted treatment of their structure at a microscale level, e.g., by thermal treatment or infusion of a substance (component) to modify the properties of the exposed material.
As a rule, these engineering procedures are implemented when it is impossible to completely eliminate the stochastic component of the process; this component is related to both, the random external multifactor action on the worked material and the state fluctuations of structural units within its volume.
The existence of the indicated component may cause various unwanted implementations of the engineering procedure and, consequently, to a result not contemplated by the technology, including the loss of process control stability.
In our opinion, a topical problem of contemporary mathematical modeling of engineering procedures aimed at making materials with tailor-made properties, based on heat-and-mass transfer, is to develop stochastic models of such procedures. These models should allow both, identifying peculiar effects of random factors on the implemented engineering procedure and work out engineering solutions for suppressing and/or controlling such factors.
One of the approaches to solving the indicated problem relies on the local mean method and was suggested in works [1─3]. Another approach is essentially the generalized theory of Brownian motion and was developed in works [4─7].
The stochastic models of heat conduction, based on the approach from [4─7] were suggested in works [8─11].
The stochastic models of diffusion mass transfer in solids are equally as important to predicting results of engineering procedures related to the diffusion of the infused component into the worked material.
However, like in heat conduction models, in this case one usually confines to solving respective boundary problems for the diffusion equation that defines the change in the average concentration of the infused component in the worked material volume; determined by the stochasticity of boundary conditions and the fluctuant concentrations of diffusing substance in the transfer region, the stochastic component of diffusion mass transfer is not taken into account. This circumstance may significantly affect the prediction of the engineering procedure results.
In this context, 1D stochastic models of diffusion mass transfer were developed in works [12─17] for stating first-, second-, and third-order boundary conditions on the boundary of the transfer region respectively. That said, the models developed in works [12─16] did not consider the technologically critical situation when sources or runoffs of diffusing substance (diffusant) may

appear in the transfer region that are conditioned, e.g., by the chemical reaction developing synchronously with the transfer and accompanied by the release or absorption of diffusant in the transfer region.

Taking this into account, work [17] formulates in brief the stochastic model of diffusion mass transfer with sources or runoffs of diffusing substance.

This work relies on the approach developed in works [12─16] to consider in detail, unlike in [17], the 1D stochastic model of diffusion mass transfer in a limited region with sources or runoffs of diffusing substance in the transfer region with third-order stochastic boundary conditions.

The work is structured as follows.

Section 2 is "Materials and Methods": it provides the formulation of the stochastic model of diffusion mass transfer (2.1) and the equations derived for the multidimensional probability density of the concentration distribution of diffusing substance in the transfer region for the discrete set of physically infinitesimal partition volumes of the transfer region, in which the local quasi-equilibrium is observed (2.2).

Section 3 is "Results": it provides system of equations (3.1) and formulates the boundary conditions for the unary function of the concentration distribution of diffusing substance (3.2), and also defines the physical parameters included in system of equations (3.3).

Section 4 is "Discussion": it provides the discrete equations for central concentration moments (4.1), continual equations for the average concentration and dispersion of diffusing substance, and formulates the boundary problems for the average concentration and dispersion of diffusing substance in case of sources or runoffs (4.2). Section 4.3 generalizes the model for 2D and 3D cases and formulates the approach to defining the parameters of physically infinitesimal volume. The conclusion is made in Section 5.

2. Materials and Methods

2.1 Formulation of the stochastic model of diffusion mass transfer. According to [12─17], assume that the region of the diffusion mass transfer of the component infused in the material is some finite interval along a number axis (e.g., thin rod of length *L* and cross-section area *s*, with an impermeable side surface).

Let us split this region in n fractional intervals. The length of each of them is equal to the value of Λ, where Λ is the standard size of physically infinitesimal volume within which the concentration can be considered constant (the definition of Λ will be given below).

Let us introduce the dimensionless time as $\tau = Dt/\Lambda^2$, where *D* is the coefficient of the diffusion of the infused component in the saturated material and *t* is the time.

Then the concentration distribution of the component infused in the material in the transfer region can be characterize using the vector $\bar{C} = (C_1, C_2, ..., C_n)$, where C_i is the diffusant concentration (density) defined as the number N_i of diffusant particles in the physically infinitesimal volume V_{ph} in the i^{th} fractional interval in relation to the total number N of particles in the indicated volume, i.e., $C_i = N_i / N$. That said, $C_i \in [C_{\min}, C_{\max}], i = 1, ..., n,$ where $C_{\min}, C_{\max}$ are the minimum and the maximum diffusant concentration, respectively. The intervals with numbers $i = 1$ and $i = n$ are boundary.

The density of probability $P(\bar{C}, \tau)$ indicating that the concentration distribution in the transfer region in the dimensionless time instant τ will be characterized by the vector $\bar{C} = (C_1, C_2, ..., C_n)$ can be recorded like in [1-5] as

$$P(\bar{C}, \tau) = \left\langle \prod_{i=1}^{n} \delta\left(C_i - \Theta_i(\tau)\right) \right\rangle, \tag{1}$$

where the averaging in equation (1) is performed for the ensemble of representations of a random concentration field.

In this case $\delta\left(C_i - \Theta_i(\tau)\right), i = 1, ..., n$ is the Delta function, $\Theta_i(\tau)$ are the values of the random concentration field $\Theta(x, \tau)$ in the i^{th} fractional interval; these values form the *n*D Markovian process $\bar{\Theta} = (\Theta_1(\tau), \Theta_2(\tau), ..., \Theta_n(\tau))$ compliant with the following system of stochastic differential equations:

$$d\Theta_i(\tau)/d\tau = \left(\Theta_{i-1}(\tau) - 2\Theta_i(\tau) + \Theta_{i+1}(\tau)\right) + (\Lambda/D)\left(f_{i-1}\left(\bar{\Theta}(\tau), \tau\right) - f_i\left(\bar{\Theta}(\tau), \tau\right)\right)$$
$$+ \left(\Lambda^2/D\right)\left(Q_i\left(\bar{\Theta}(\tau), \tau\right) + g_i\left(\bar{\Theta}(\tau), \tau\right)\right). \tag{2}$$

Equation (2) stems from the law of conservation of mass applied in the presence of a source or runoff with the capacity $Q_i\left(\bar{\Theta}(\tau), \tau\right) + g_i\left(\bar{\Theta}(\tau), \tau\right)$, with the random component $g_i\left(\bar{\Theta}(\tau), \tau\right)$; the discrete representation of the diffusion flow density used to record this equation according to [1–4] is

$$J_i = -(D/\Lambda)\left(\Theta_{i+1}(\tau) - \Theta_i(\tau)\right) + f_i\left(\bar{\Theta}, \tau\right),$$
$$i = 1, ..., n-1. \tag{3}$$

The functions $\Theta_1(\tau), \Theta_n(\tau)$ are the values of the random diffusant concentration field $\Theta(x, \tau)$ in the boundary fractional intervals with the numbers $i = 1$ and $i = n$, respectively, and meet the following boundary conditions:

$$-(\beta_1\Lambda/D)\left(\Theta_1(\tau) - \varphi_1(\tau)\right) + (\Lambda/D)\left(\beta_1 f_0\left(\bar{\Theta}(\tau), \tau\right) - f_1\left(\bar{\Theta}(\tau), \tau\right)\right) +$$
$$+ \left(\Theta_2(\tau) - \Theta_1(\tau)\right) = 0, \tag{4}$$

$$-(\beta_2\Lambda/D)\left(\Theta_n(\tau)-\varphi_2(\tau)\right)+(\Lambda/D)\left(\beta_2 f_n\left(\bar\Theta(\tau),\tau\right)+f_{n-1}\left(\bar\Theta(\tau),\tau\right)\right)+$$
$$+\left(\Theta_{n-1}(\tau)-\Theta_n(\tau)\right)=0, \quad (5)$$

where β_1 and β_2 are the coefficients of the mass exchange between the transfer region and the environment through the left (x=0) and the right (x=l) boundary, respectively; $\varphi_1(\tau)$ and $\varphi_2(\tau)$ are the determined (average) diffusant values at the left (x=0) and the right (x=l) boundary of the mass transfer region, respectively.

According to [12–17], the random functions $(n+1)$ of the variable $f_i\left(\bar\Theta,\tau\right)$ meet the following conditions: a) $f_i\left(\bar C,\tau\right)$ is the random Gaussian field in the $(n+1)$D space $\left(\bar C,\tau\right)$; b) $\left\langle f_i\left(\bar C,\tau\right)\right\rangle=0,\ i=0,2,...,n$.

2.2. Deriving the stochastic model equations. The equation derived by differentiating (1) against τ and according to [12–17] is

$$\partial P\left(\bar{\mathrm C},\tau\right)/\partial\tau=-\sum_{k=2}^{n-1}\partial/\partial C_k\left[\Delta C_k+Q_k^d\left(\bar C,\tau\right)\right]P\left(\bar{\mathrm C},\tau\right)-(\beta_1\Lambda/D)\varphi_1(\tau)\partial/\partial C_1 P\left(\bar{\mathrm C},\tau\right)$$
$$+(\Lambda/D)\sum_{k=2}^{n-1}\partial/\partial C_k\left(\left\langle\left(f_k\left(\bar\Theta(\tau),\tau\right)-f_{k-1}\left(\bar\Theta(\tau),\tau\right)-\Lambda g_k\left(\bar\Theta(\tau),\tau\right)\right)\delta\left(\bar{\mathrm C}-\bar\Theta(\tau)\right)\right\rangle\right)+$$
$$+\partial/\partial C_1\left(\left((1+\beta_1\Lambda/D)C_1-C_2\right)P\left(\bar{\mathrm C},\tau\right)\right)-\partial/\partial C_1\left\langle d\theta_1/d\tau\,\delta\left(\bar{\mathrm C}-\bar\Theta(\tau)\right)\right\rangle+$$
$$+\partial/\partial C_n\left(\left(\left((1+\beta_2\Lambda/D)C_n-C_{n-1}\right)P\left(\bar{\mathrm C},\tau\right)\right)\right)-\partial/\partial C_n\left\langle d\theta_n/d\tau\,\delta\left(\bar{\mathrm C}-\bar\Theta(\tau)\right)\right\rangle+$$
$$+(\Lambda/D)\partial/\partial C_1\left(\left\langle\left(f_1\left(\bar\Theta(\tau),\tau\right)-\beta_1 f_0\left(\bar\Theta(\tau),\tau\right)\right)\delta\left(\bar{\mathrm C}-\bar\Theta(\tau)\right)\right\rangle\right)-$$
$$-(\Lambda/D)\partial/\partial C_n\left(\left\langle\left(\beta_2 f_n\left(\bar\Theta(\tau),\tau\right)+f_{n-1}\left(\bar\Theta(\tau),\tau\right)\right)\delta\left(\bar{\mathrm C}-\bar\Theta(\tau)\right)\right\rangle\right)- \quad (6)$$
$$-(\beta_2\Lambda/D)\varphi_2(\tau)\partial/\partial C_n P\left(\bar{\mathrm C},\tau\right).$$

In this case $\delta\left(\bar C-\bar\Theta(\tau)\right)=\prod_{i=1}^{n}\delta\left(C_i-\Theta_i(\tau)\right)$, $\Delta C_k=C_{k-1}-2C_k+C_{k+1}$, $Q_k^d=\Lambda^2 Q_k/D$.

The expressions included in equation (6) are

$$A_k=\left\langle\left(f_k\left(\bar\Theta(\tau),\tau\right)-f_{k-1}\left(\bar\Theta(\tau),\tau\right)\right)\delta\left(\bar{\mathrm C}-\bar\Theta(\tau)\right)\right\rangle,\ k=2,...,n-1,$$
$$A_1=\left\langle\left(f_1\left(\bar\Theta(\tau),\tau\right)-\beta_1 f_0\left(\bar\Theta(\tau),\tau\right)\right)\delta\left(\bar{\mathrm C}-\bar\Theta(\tau)\right)\right\rangle,$$
$$A_n=\left\langle\left(\beta_2 f_n\left(\bar\Theta(\tau),\tau\right)+f_{n-1}\left(\bar\Theta(\tau),\tau\right)\right)\delta\left(\bar{\mathrm C}-\bar\Theta(\tau)\right)\right\rangle; \quad (7)$$

the quantity they contain under the sign of averaging by the ensemble of representations of the random concentration field $\Theta(x,\tau)$ is the correlation of the random quantities $f_k\left(\bar\Theta(\tau),\tau\right)$ with the density $\delta\left(\bar C-\bar\Theta(\tau)\right)$ that depends itself on solving the system of (2), (4), and (5), and, therefore, is functional of the random process $\left(f_0\left(\bar\Theta(\tau),\tau\right),f_2\left(\bar\Theta(\tau),\tau\right),...,f_n\left(\bar\Theta(\tau),\tau\right)\right)$. This correlation is calculated by the method exposed in [4, 6, 7].

According to [4, 6, 7, 12–17] and taking into account that the functions $\Theta_i(\tau)$ depend only on the values of $f_i\left(\bar\Theta(\tau'),\tau'\right)$, preceding the time τ, where $\tau'<\tau$, we have

$$A_k=\left\langle\left(f_k\left(\bar\Theta(\tau),\tau\right)-f_{k-1}\left(\bar\Theta(\tau),\tau\right)\right)\delta\left(\bar C-\bar\Theta(\tau)\right)\right\rangle=$$

$$= \int d\bar{C}' \int_0^{\tau} d\eta \left\langle \left(f_k\left(\bar{\mathrm{C}},\tau\right) - f_{k-1}\left(\bar{\mathrm{C}},\tau\right)\right) \cdot f_l\left(\bar{\mathrm{C}}',\eta\right) \right\rangle \left\langle \frac{\delta}{\delta f_l\left(\bar{\mathrm{C}}',\eta\right)} \delta\left(\bar{C} - \bar{\Theta}(\tau)\right) \right\rangle \quad (8)$$

and then

$$A_k = -\int d\bar{C}' \int_0^{\tau} d\eta \left\langle \left(f_k\left(\bar{\mathrm{C}},\tau\right) - f_{k-1}\left(\bar{\mathrm{C}},\tau\right)\right) \cdot f_l\left(\bar{C}',\eta\right) \right\rangle \frac{\partial}{\partial C_j} \left\langle \frac{\delta\Theta_j(\tau)}{\delta f_l\left(\bar{C}',\eta\right)} \delta\left(\bar{C} - \bar{\Theta}(\tau)\right) \right\rangle$$
$$k = 2,...,n-1, \quad (9)$$

where $d\bar{C}' = \prod_{k=2}^{n-1} dC'_k$; the integration for each of these variables is performed hereinafter along the section $\left[C_{\min}, C_{\max}\right]$. From this point onward, the twice repeated indices are used to imply the summation.
According to [7, 12–17], assume that

$$\left\langle f_k\left(\bar{C},\tau\right) \cdot f_l\left(\bar{C}',\eta\right) \right\rangle = 2B_{kl}\left(\bar{C},\tau,\bar{C}',\eta\right)\delta\left(\tau-\eta\right)$$
$$, k,l = 1,2,...,n-1. \quad (10)$$

The correlations $\left\langle f_0(\tau) \cdot f_0(\eta) \right\rangle, \left\langle f_n(\tau) \cdot f_n(\eta) \right\rangle$ are found as

$$\left\langle f_0(\tau) \cdot f_0(\eta) \right\rangle = 2B_0(\tau)\delta(\tau-\eta),$$
$$\left\langle f_n(\tau) \cdot f_n(\eta) \right\rangle = 2B_n(\tau)\delta(\tau-\eta). \quad (11)$$

The variation derivatives $\delta\Theta_j(\tau) / \delta f_l\left(\bar{C}',\eta\right)$ included in (9) are found from the following equation

$$\Theta_i(\tau) = \Theta_i(0) + \int_0^{\tau} d\xi \int d\bar{C}'' \left[\Delta C_i'' + (\Lambda/D)\left(f_{i-1}\left(\bar{C}'',\eta\right) - f_i\left(\bar{C}'',\eta\right)\right)\right] \delta\left(\bar{C}'' - \bar{\Theta}(\eta)\right) +$$
$$+ \int_0^{\tau} d\xi \int d\bar{C}'' \left[Q_i^d\left(\bar{C}'',\tau\right) + \left(\Lambda^2/D\right) g_i\left(\bar{C}'',\tau\right)\right] \delta\left(\bar{C}'' - \bar{\Theta}(\eta)\right), i = 2,...,n-1, \quad (12)$$

derived by integrating equation (2) and also from equations (4) and (5) represented as

$$\Theta_1(\tau) = \int_0^{\tau} \delta(\tau-\xi) d\xi \int d\bar{C}'' \left[C_2'' - (\Lambda/D)\left(f_1\left(\bar{C}'',\xi\right) - \beta_1 f_0\left(\bar{C}'',\xi\right)\right) + \right.$$
$$\left. + \left(\beta_1\Lambda/D\right)\varphi_1(\xi)\right] \delta\left(\bar{C}'' - \bar{\Theta}(\xi)\right)\left(1/\left(1 + \left(\beta_1\Lambda/D\right)\right)\right), \quad (13)$$

$$\Theta_n(\tau) = \int_0^{\tau} \delta(\tau-\xi) d\xi \int d\bar{C}'' \left[C_{n-1}'' + (\Lambda/D)\left(f_{n-1}\left(\bar{C}'',\xi\right) + \beta_2 f_n\left(\bar{C}'',\xi\right)\right) + \right.$$
$$\left. + \left(\beta_2\Lambda/D\right)\varphi_2(\xi)\right] \delta\left(\bar{C}'' - \bar{\Theta}(\xi)\right)\left(1/\left(1 + \left(\beta_2\Lambda/D\right)\right)\right)$$
$$. \quad (14)$$

If to process these equations via the operator $\delta/\delta f_l\left(\bar{C}',\eta\right)\ (\eta < \tau)$ and take into account that $\delta f_i\left(\bar{C},\tau\right) / \delta f_k\left(\bar{C}',\eta\right) = \delta\left(\bar{C} - \bar{C}'\right)\delta(\tau-\eta)\delta_{ik}$, the result will be

$$\delta\Theta_i(\tau) / \delta f_l\left(\bar{C}',\eta\right) = (\Lambda/D)\left(\delta_{i-1l} - \delta_{il}\right)\delta\left(\bar{C}' - \bar{\Theta}(\eta)\right) - \Psi_{il}(\tau,\eta), \quad (15)$$

where $\Psi_{il}(\tau,\eta) = \int_{\eta}^{\tau} d\xi \int d\bar{C}'' \left[\Delta C_i'' + \right.$

$$\left. + (\Lambda/D)\left(f_i\left(\bar{C}'',\xi\right) - f_{i-1}\left(\bar{C}'',\xi\right)\right)\right] \partial/\partial C_k'' \delta\left(\bar{C}'' - \bar{\Theta}(\eta)\right) \delta\Theta_k(\xi) / \delta f_l\left(\bar{C}',\eta\right) +$$

$$+\int_{\eta}^{\tau} d\xi \int d\bar{C}''\left[Q_i^d\left(\bar{C}'',\tau\right)+\left(\Lambda^2/D\right)g_i\left(\bar{C}'',\tau\right)\right]\partial/\partial C_k''\delta\left(\bar{C}''-\bar{\Theta}(\eta)\right)\delta\Theta_k(\xi)/\delta f_l\left(\bar{C}',\eta\right)$$

$i=2,...,n-1, l=1,...,n-1$. Here δ_{kl} is the Kronecker index.

The result from equations (13) and (14) is similarly derived as

$$\delta\Theta_1(\tau)/\delta f_l\left(\bar{C}',\eta\right)=\left(\left(\Lambda/D\right)/\left(1+\left(\beta_1\Lambda/D\right)\right)\right)\left(\beta_1\delta_{0l}-\delta_{1l}\right)\delta\left(\bar{C}'-\bar{\Theta}(\eta)\right)-\Psi_{1l}(\tau,\eta)$$

$$\Psi_{1l}(\tau,\eta)=\int_{\eta}^{\tau}\delta(\tau-\xi)d\xi\int d\bar{C}''\left[C_2''+\left(\Lambda/D\right)\left(\beta_1 f_0\left(\bar{C}'',\xi\right)-f_1\left(\bar{C}'',\xi\right)\right)+\right.$$

$$\left.+\left(\beta_1\Lambda/D\right)\varphi_1(\xi)\right]\partial/\partial C_k''\delta\left(\bar{C}''-\bar{\Theta}(\eta)\right)\delta\Theta_k(\xi)/\delta f_l\left(\bar{C}',\eta\right)\left(1/\left(1+\left(\beta_1\Lambda/D\right)\right)\right)$$

$$\delta\Theta_n(\tau)/\delta f_l\left(\bar{C}',\eta\right)=\left(\left(\Lambda/D\right)/\left(1+\left(\beta_1\Lambda/D\right)\right)\right)\left(\beta_2\delta_{nl}+\delta_{n-1l}\right)\delta\left(\bar{C}'-\mathbf{\Theta}(\eta)\right)-\Psi_{nl}(\tau,\eta)$$

$$\Psi_{nl}(\tau,\eta)=\int_{\eta}^{\tau}\delta(\tau-\xi)d\xi\int d\bar{C}''\left[C_{n-1}''+\left(\Lambda/D\right)\left(\beta_2 f_n\left(\bar{C}'',\xi\right)+f_{n-1}\left(\bar{C}'',\xi\right)\right)+\right.$$

$$\left.+\left(\beta_2\Lambda/D\right)\varphi_2(\xi)\right]\partial/\partial C_k''\delta\left(\bar{C}''-\bar{\Theta}(\eta)\right)\delta\Theta_k(\xi)/\delta f_l\left(\bar{C}',\eta\right)\left(1/\left(1+\left(\beta_2\Lambda/D\right)\right)\right)$$

Then, the result obtained according to [7, 12─17] and taking account of the type of equations (2), (4), (5) and conditions (10)─(11) is

$$A_k=\left(\Lambda/D\right)\sum_{j=1}^{n}\frac{\partial}{\partial C_j}\left(B_{k,j}\left(\bar{C},\tau\right)-B_{(k-1),j}\left(\bar{C},\tau\right)\right)P\left(\bar{C},\tau\right)-$$
$$-\left(\Lambda/D\right)\sum_{j=1}^{n}\frac{\partial}{\partial C_{j+1}}\left(B_{k,j}\left(\bar{C},\tau\right)-B_{(k-1),j}\left(\bar{C},\tau\right)\right)P\left(\bar{C},\tau\right), \quad (16)$$

$$A_1=\left(\Lambda/D\right)\left(1/\left(1+\beta_1\Lambda/D\right)\left(\frac{\partial}{\partial C_1}\left(B_{11}+\beta_1^2B_0\right)+\frac{\partial}{\partial C_n}B_{1(n-1)}\right)\right)P\left(\bar{C},\tau\right)+$$
$$+\left(\Lambda/D\right)\left(\sum_{k=2}^{n-1}\frac{\partial}{\partial C_k}B_{1k}-\sum_{k=1}^{n-1}\frac{\partial}{\partial C_{k+1}}B_{1k}\right)P\left(\bar{C},\tau\right), \quad (17)$$

$$A_n=\left(\Lambda/D\right)\left(-1/\left(1+\beta_2\Lambda/D\right)\left(\frac{\partial}{\partial C_n}\left(B_{(n-1)(n-1)}+\beta_2^2B_n\right)+\frac{\partial}{\partial C_1}B_{(n-1)1}\right)\right)P\left(\bar{C},\tau\right)+$$
$$+\left(\Lambda/D\right)\left(\sum_{k=2}^{n-1}\frac{\partial}{\partial C_k}B_{(n-1)k}-\sum_{k=1}^{n-1}\frac{\partial}{\partial C_{k+1}}B_{(n-1)k}\right)P\left(\bar{C},\tau\right). \quad (18)$$

In equations (16)–(18) $B_{ik}\left(\bar{C},\tau,\bar{C},\tau\right)=B_{ik}\left(\bar{C},\tau\right)$. The values of B_{kl} will be found further on.

The correlations $G_k=\left\langle g_k\left(\bar{\Theta}(\tau),\tau\right)\delta\left(\bar{C}-\bar{\Theta}(\tau)\right)\right\rangle$ are calculated in a similar manner. We have

$$G_k=-\int d\bar{C}'\int_0^{\tau}d\eta\left\langle\left(g_k\left(\bar{C},\tau\right)\right)\cdot g_l\left(\bar{C}',\eta\right)\right\rangle\frac{\partial}{\partial C_j}\left\langle\frac{\delta\Theta_j(\tau)}{\delta g_l\left(\bar{C}',\eta\right)}\delta\left(\bar{C}-\bar{\Theta}(\tau)\right)\right\rangle, \quad (19)$$

$k=2,...,n-1.$

The result of equation (12) is

$$\frac{\delta\Theta_j(\tau)}{\delta g_l\left(\bar{C}',\eta\right)}=\left(\Lambda^2/D\right)\delta_{jl}\delta\left(\bar{C}'-\bar{\Theta}(\eta)\right)\delta(\tau-\eta)-\Phi_{jl}(\tau,\eta)$$, where

$$\Phi_{jl}(\tau,\eta)=\int_{\eta}^{\tau}d\xi\int d\bar{C}''\left[\Delta C_i''+\right.$$

$$+(\Lambda/D)\left(f_i(\bar{C}'',\xi)-f_{i-1}(\bar{C}'',\xi)\right)\Big]\partial/\partial C_k''\delta\left(\bar{C}''-\bar{\Theta}(\eta)\right)\delta\Theta_k(\xi)\big/\delta g_l(\bar{C}',\eta)+$$

$$+\int_{\eta}^{\tau}d\xi\int d\bar{C}''\left[Q_i^d(\bar{C}'',\tau)+\left(\Lambda^2/D\right)g_i(\bar{C}'',\tau)\right]\partial/\partial C_k''\delta\left(\bar{C}''-\bar{\Theta}(\eta)\right)\delta\Theta_k(\xi)\big/\delta g_l(\bar{C}',\eta)$$

Considering that $\left\langle g_k(\bar{C},\tau)\cdot g_l(\bar{C}',\eta)\right\rangle=2D_{kl}(\bar{C},\tau,\bar{C}',\eta)\delta(\tau-\eta)$, this result is reduced to

$$G_k=-\left(\Lambda^2/D\right)\sum_{j=1}^{n-1}\partial/\partial C_jD_{kj}P(\bar{C},\tau)\ , \tag{20}$$

where $D_{kl}=D_{kl}(\bar{C},\tau,\bar{C},\tau)=D_{kl}(\bar{C},\tau)$

The equation for $P(\bar{C},\tau)$ derived by substituting equations (16) – (18) to (6) is

$$\begin{aligned}\partial P(\bar{C},\tau)\big/\partial\tau=&-\sum_{k=2}^{n-1}\partial/\partial C_k\left[\left(\Delta C_k+Q_k^d\right)P(\bar{C},\tau)\right]-(\beta_1\Lambda/D)\varphi_1(\tau)\partial/\partial C_1P(\bar{C},\tau)-\\&-(\beta_2\Lambda/D)\varphi_2(\tau)\partial/\partial C_nP(\bar{C},\tau)+\sum_{k=2}^{n-1}\left((\Lambda/D)\partial A_k/\partial C_k-\left(\Lambda^2/D\right)\partial G_k\big/\partial C_k\right)-\\&-\partial\big/\partial C_1\left((C_2-C_1)P(\bar{C},\tau)\right)+\partial\big/\partial C_n\left((C_n-C_{n-1})P(\bar{C},\tau)\right)+(\Lambda/D)\partial A_1/\partial C_1+\\&+(\Lambda/D)(\beta_1\partial/\partial C_1C_1+\beta_2\partial/\partial C_nC_n)P(\bar{C},\tau)-(\Lambda/D)\partial A_n/\partial C_n-\\&-\partial/\partial C_1\left\langle d\theta_1/d\tau\,\delta\left(\bar{C}-\bar{\Theta}(\tau)\right)\right\rangle-\partial/\partial C_n\left\langle d\theta_n/d\tau\,\delta\left(\bar{C}-\bar{\Theta}(\tau)\right)\right\rangle.\end{aligned} \tag{21}$$

3.Results

3.1. Boundary conditions for $P(\bar{C},\tau)$. It follows from (1) that $P(\bar{C},\tau)$ meets the norming condition $\int P(\bar{C},\tau)d\bar{C}=1$, где $d\bar{C}=\prod_{i=1}^{n}dC_i$, and the integration by each variable C_i is performed in the interval $[C_{\min},C_{\max}]$. Consequently, if now to integrate equation (21) for all $C_i\in[C_{\min},C_{\max}],i=1,...,n,$ then the left part of this equation will be zero and the expression in the right part will be too cluttered to record here. This expression consists of summands with quantities of the following kind:

$$\begin{aligned}&\int_{C_{\min}}^{C_{\max}}\left(P_2(C_k=C_{\max},C_{k\pm1},\tau)-P_2(C_k=C_{\min},C_{k\pm1},\tau)\right)C_{k\pm1}dC_{k\pm1},P_1(C_i=C_{\max},\tau),\\&P_1(C_i=C_{\min},\tau)P_2(C_k=C_{\max},C_{k\pm1}=C_{\max},\tau),P_2(C_k=C_{\max},C_{k\pm1}=C_{\min},\tau),\\&P_2(C_k=C_{\min},C_{k\pm1}=C_{\max},\tau),P_2(C_k=C_{\min},C_{k\pm1}=C_{\min},\tau),\partial\big/\partial C_iP_1(C_k=C_{\max},\tau),\\&\partial\big/\partial C_iP_1(C_k=C_{\min},\tau).\end{aligned} \tag{22}$$

In this case $P_1(C_i,\tau)$ is the probability that the concentration in the i^{th} partial interval at the time instant τ will belong to the range (C_i,C_i+dC_i) and $P_2(C_i,C_k,\tau)$ is the probability that the concentrations in the i^{th} and k^{th} partial intervals will belong to the ranges (C_i,C_i+dC_i) and (C_k,C_k+dC_k), respectively. The function $P_1(C_i,\tau)$ is expressed via the function

$P\left(\bar{C},\tau\right)$ as

$$P_1\left(C_i,\tau\right)=\int P\left(\bar{C},\tau\right)dC_1dC_2...dC_{i-1}dC_{i+1}...dC_{n-1}=\int\limits_{C_{\min}}^{C_{\max}}P_2\left(C_i,C_k,\tau\right)dC_k \quad (23)$$

Consequently, the binary diffusant distribution density $P_2\left(C_i,C_k,\tau\right)$ is found as

$$P_2\left(C_i,C_k,\tau\right)=\int P\left(\bar{C},\tau\right)dC_1dC_2...dC_{i-1}dC_{i+1}...dC_{k-1}dC_{k+1}...dC_n \quad (24)$$

If now to require that

$$\int\limits_{C_{\min}}^{C_{\max}}P_2\left(C_i=C_{\max},C_k,\tau\right)dC_k=\int\limits_{C_{\min}}^{C_{\max}}P_2\left(C_i=C_{\min},C_k,\tau\right)dC_k=0,\ i,k=1,...,n,$$

and, then, $P_1\left(C_k=C_{\min},\tau\right)=P_1\left(C_k=C_{\max},\tau\right)=0$, $k=1,...,n,$ by virtue of (23). As a result, all the summands with the quantities indicated in (22) will become zero but for those with the derivatives $\partial/\partial C_iP_1\left(C_k=C_{\max},\tau\right),\partial/\partial C_iP_1\left(C_k=C_{\min},\tau\right).$, $k=1,...,n,$. As a consequence, to meet the norming condition, it is necessary to meet the following conditions:

$$\partial/\partial C_iP_1\left(C_k=C_{\max},\tau\right)=0,$$
$$\partial/\partial C_iP_1\left(C_k=C_{\min},\tau\right)=0,k=1,...,n. \quad (25)$$

$P_2\left(C_i=C_{\max},C_k,\tau\right)=P_2\left(C_i=C_{\min},C_k,\tau\right)=0$, where $C_k\in\left[C_{\min},C_{\max}\right], i,k=1,...,n,$ this will lead to the equations

$$P_2\left(C_i=C_{\max},C_k,\tau\right)=P_2\left(C_i=C_{\min},C_k,\tau\right)=0,\ C_k\in\left[C_{\min},C_{\max}\right],i,k=1,...,n. \quad (26)$$

3.2. Equation for the unary distribution function $P_1\left(C_i,\tau\right)$.

The equations derived by following [12–17] and integrating equation (21) for all the variables C_k but for $C_i, i\neq k$, and taking into account boundary conditions (25) and (26), are

$$\partial P_1\left(C_i,\tau\right)/\partial\tau=\left(\Lambda/D\right)^2\left(B_i+\Lambda^2D_i\right)\partial^2P_1\left(C_i,\tau\right)/\partial C_i^2-\partial/\partial C_i\,Q_i^d\left(C_i\right)P_1\left(C_i,\tau\right)-$$
$$-\partial/\partial C_i\left(\int\limits_{C_{\min}}^{C_{\max}}P_2\left(C_i,C_{i-1},\tau\right)C_{i-1}dC_{i-1}-2C_iP_1\left(C_i,\tau\right)+\int\limits_{C_{\min}}^{C_{\max}}P_2\left(C_i,C_{i+1},\tau\right)C_{i+1}dC_{i+1}\right)$$
$$i=2,...,n-1,\ \text{где}\ B_i=B_{ii}-B_{(i-1)i}+B_{(i-1)(i-1)}-B_{i(i-1)},D_i=D_{ii}.. \quad (27)$$

$$\partial P_1\left(C_1,\tau\right)/\partial\tau=-\partial/\partial C_1\left(\int\limits_{C_{\min}}^{C_{\max}}P_2\left(C_1,C_2,\tau\right)C_2dC_2-C_1P_1\left(C_1,\tau\right)\right)+$$
$$+\left(\beta_1\Lambda/D\right)\partial/\partial C_1\left(C_1-\varphi_1\left(\tau\right)\right)P_1\left(C_1,\tau\right)-\partial/\partial C_1\left\langle d\theta_1/d\tau\,\delta\left(C_1-\Theta_1\left(\tau\right)\right)\right\rangle \quad (28)$$
$$+\left(\left(\left(\Lambda/D\right)^2/\left(1+\beta_1\Lambda/D\right)\right)\partial^2/\partial C_1^2\left(\left(B_{11}+\beta_1^2B_0\right)\right)\right)P_1\left(C_1,\tau\right)$$

$$\partial P_1\left(C_n,\tau\right)/\partial\tau=-\partial/\partial C_n\left(\int\limits_{C_{\min}}^{C_{\max}}P_2\left(C_{n-1},C_n,\tau\right)C_{n-1}dC_{n-1}-C_nP_1\left(C_n,\tau\right)\right)+$$
$$+\left(\beta_2\Lambda/D\right)\partial/\partial C_n\left(C_n-\varphi_2\left(\tau\right)\right)P_1\left(C_n,\tau\right)-\partial/\partial C_n\left\langle d\theta_n/d\tau\,\delta\left(C_n-\Theta_n\left(\tau\right)\right)\right\rangle+ \quad (29)$$
$$+\left(\left(\left(\Lambda/D\right)^2/\left(1+\beta_2\Lambda/D\right)\right)\partial^2/\partial C_n^2\left(\left(B_{(n-1)(n-1)}+\beta_2^2B_n\right)\right)\right)P_1\left(C_n,\tau\right)$$

When deriving (27) it is taken that the capacity of the source or runoff of diffusant in the i^{th} fractional interval depends only on the diffusant concentration in this interval.

Thus the equations for the unary distribution function $P_1\left(C_i,\tau\right)$ contain the binary distribution functions $P_2(C_i, C_k, \tau)$. In their respect, the equations for the binary distribution function $P_2(C_i, C_k, \tau)$ will contain the triple distribution functions $P_3(C_i, C_k, C_l, \tau)$, etc.

3.3. Finding the coefficients of diffusions in the concentration space. The unknown quantities B_i $i = 2,...,n-1$, B_{11}, $B_{(n-1)(n-1)}$ included in equations (27)–(29) were defined in [12–17] on condition that the function $P(\bar{C}, \tau)$ as the solution of (27)–(29) for the state of thermodynamic equilibrium coincided with the thermodynamic probability density for the concentration fluctuations $P^{(0)}(C)$

$$P^{(0)}(C) = A\exp\left[-N\left(C - \langle C\rangle\right)^2 / 2\langle C\rangle\right], \quad (30)$$

where A is the norming constant, N is the number of solvent particles in the volume $V = \Lambda^3$ of the mass transfer region, $\langle C\rangle$ is the average concentration of the infused component in this volume [18]. In the state of thermodynamic equilibrium it follows from (27) that $\partial P_1(C_i, \tau)/\partial\tau = 0$, $Q_i^d(C_i) = 0$ и $D_i = 0$.

Then the equation derived from (27) in equilibrium is

$$(\Lambda/D)^2 B_i\, dP_1(C_i)/dC_i - \int_{C_{\min}}^{C_{\max}} P_2(C_i, C_{i-1}) C_{i-1} dC_{i-1} + 2C_i P_1(C_i) - \int_{C_{\min}}^{C_{\max}} P_2(C_i, C_{i+1}) C_{i+1} dC_{i+1} = 0, i = 2,...,n-1. \quad (31)$$

To ensure that (31) is the same as (30), one needs to meet the following condition in equilibrium

$$P_2(C_i, C_{i\pm1}, \tau) = P_1(C_i) P_1(C_{i\pm1}), \quad (32)$$

that is, we have no correlations in equilibrium.

Then equation (31) is transformed as

$$(\Lambda/D)^2 B_i\, dP_1(C_i)/dC_i + 2\left(C_i - \langle C_i\rangle\right)P_1(C_i) = 0 \quad (33)$$

The function $P^{(0)}(C)$ meets the equation

$$dP^{(0)}(C)/dC + \left(N/\langle C\rangle\right)\left(C - \langle C\rangle\right)P^{(0)}(C) = 0 \quad (34)$$

The result of comparing (33) and (34) is

$B_i = 2\mu\langle C_i\rangle$, где $\mu = (D/\Lambda)^2/N$, , $i = 2,...,n-1$.

Considering term (32), equations (28) and (29) are transformed as

$$\left(\frac{\Lambda}{D}\right)^2 B_{11}\frac{dP(C_1)}{dC_1} + \left(C_1 - \langle C_1\rangle\right)P(C_1) - \frac{(\Lambda/D)^2}{(1+\beta_1\Lambda/D)}\frac{dP(C_1)}{dC_1}\left(\frac{\beta_1\Lambda}{D}B_{11} - \beta_1^2 B_0\right) = 0$$

$$\left(\frac{\Lambda}{D}\right)^2 B_{(n-1)(n-1)}\frac{dP_1(C_n)}{dC_n} + \left(C_n - \langle C_n\rangle\right)P_1(C_n) - \frac{(\Lambda/D)^2}{(1+\beta_2\Lambda/D)}\frac{dP(C_n)}{dC_n}\left(\frac{\beta_2\Lambda}{D}B_{(n-1)(n-1)} - \beta_2^2 B_n\right) = 0.$$

If to set to zero the first two summands in these equations, the result will be

$$B_{11} = \mu\langle C_1\rangle, B_{(n-1)(n-1)} = \mu\langle C_n\rangle \quad (35)$$

Therefore, it will be possible to solve the recorded equations in equilibrium given that the following conditions are met:

$$\frac{\beta_1\Lambda}{D}B_{11} - \beta_1^2 B_0 = 0, \frac{\beta_2\Lambda}{D}B_{(n-1)(n-1)} - \beta_2^2 B_n = 0. \quad (36)$$

$$B_{11} = \mu\langle C_1\rangle, B_{(n-1)(n-1)} = \mu\langle C_n\rangle \quad (37)$$

The unknown quantities B_0 and B_n included in equations (36) and (37) are found from the stochastic equations for the substrate concentration $\Theta_{c,1}$ and $\Theta_{c,n}$ to the left, x=0, and to the right x=l, of the transfer region boundary [14]:

$$\Theta_{c,1} = \varphi_1(\tau) + f_0(\tau), \Theta_{c,n} = \varphi_2(\tau) + f_n(\tau).$$

Assume that

$$\left\langle\left(\Theta_{c,1}(\tau) - \varphi_1(\tau)\right)\left(\Theta_{c,1}(\eta) - \varphi_1(\eta)\right)\right\rangle = \sigma_1^2(\tau)\delta(\tau-\eta) = \langle f_0(\tau) f_0(\eta)\rangle = 2B_0(\tau)\delta(\tau-\eta)$$

$$\left\langle\left(\Theta_{c,2}(\tau) - \varphi_2(\tau)\right)\left(\Theta_{c,2}(\eta) - \varphi_2(\eta)\right)\right\rangle = \sigma_2^2(\tau)\delta(\tau-\eta) = \langle f_n(\tau) f_n(\eta)\rangle = 2B_n(\tau)\delta(\tau-\eta)$$

.

It follows from these equations that

$$B_0(\tau) = \sigma_1^2(\tau)/2, B_n(\tau) = \sigma_2^2(\tau)/2, \quad (38)$$

where σ_1 and σ_2 are the average square deviations in the substrate concentration near the transfer region boundary from the average substrate concentration values.

Thus, in equations (28) and (29)

$$B_1 + \beta^2 B_0 = \mu\langle C_1\rangle + \beta^2\sigma_1^2(\tau)/2,$$
$$B_{n-1} + \beta^2 B_n = \mu\langle C_n\rangle + \beta^2\sigma_2^2(\tau)/2. \quad (39)$$

$B_0(\tau) = \sigma_1^2(\tau)/2, B_n(\tau) = \sigma_2^2(\tau)/2$. That said, the conditions to be met in equilibrium are $B_0 = B_{11}\Lambda/(\beta_1 D)$, $B_n = B_{(n-1)(n-1)}\Lambda/(\beta_2 D)$.

The quantities D_i are found as follows. First of all, an equation is derived from equation (2) at zero diffusion but with a source or runoff of diffusant and recorded as

$$d\Theta_i(\tau)/d\tau = (\Lambda^2/D)\left(Q_i\left(\bar{\Theta}(\tau),\tau\right) + g_i\left(\bar{\Theta}(\tau),\tau\right)\right), i = 2,...,n-1. \quad (40)$$

Let us expand the function $Q_i\left(\bar{\Theta}(\tau),\tau\right)$ in a series in powers of $\Theta_i - \langle C_{i0}\rangle$, where $\langle C_{i0}\rangle = \langle C_i(0)\rangle$ is the average initial concentration in the i^{th} interval, and confine to linear terms on the assumption that $Q_i\left(\mathbf{\Theta}_i(\tau),\tau\right) = Q_i\left(\Theta_i(\tau)\right)$. We have

$$Q_i\left(\mathbf{\Theta}(\tau),\tau\right) = Q_{i0} + Q_{i0}{}' \cdot \left(C_i - \langle C_{i0}\rangle\right), \quad (41)$$

where $Q_{i0} = Q_i\left(\langle C_i(0)\rangle\right), Q_{i0}{}' = dQ_i\left(\langle C_i(0)\rangle\right)/dC_i$.

Then equation (42) is recorded as

$$d\Psi_i(\tau)/d\tau = Q_{i0}{}' \cdot (\Lambda^2/D)\left(\Psi_i(\tau) + g_i\left(\Psi_i(\tau),\tau\right)\right), \quad (42)$$

where $\Psi_i(\tau) = \Theta_i - \langle C_{i0}\rangle + Q_{i0}/Q_{i0}{}'$.

It to follow [18], the result of (42) will be

$$\left\langle g_i\left(\Theta_i(\tau),\tau\right) g_i\left(\Theta_i(\tau),\tau\right)\right\rangle = -2Q_{i0}{}' \cdot \left\langle \Psi_i^2(\tau)\right\rangle \left(D/\Lambda^2\right)^2. \quad (43)$$

Then

$$D_i = -Q_{i0}{}' \cdot \left\langle \Psi_i^2\right\rangle \left(D/\Lambda^2\right)^2 = -Q_{i0}{}'\left(D/\Lambda^2\right)^2 \left\langle \left(\Theta_i - \langle C_{i0}\rangle + Q_{i0}/Q_{i0}{}'\right)^2\right\rangle = \quad (44)$$

$$= -Q_{i0}{}'\left(D/\Lambda^2\right)^2 \left(\left\langle C_i^2\right\rangle + \left\langle C_{i0}^2\right\rangle + \left(Q_{i0}/Q_{i0}{}'\right)^2 - 2\langle C_i\rangle\langle C_{i0}\rangle + 2\left(\langle C_i\rangle - \langle C_{i0}\rangle\right)Q_{i0}/Q_{i0}{}'\right).$$

4. Discussion

4.1. Moment function equations. Like in [12–17], equations (27)–(29) allow deriving equations for moment functions of various orders. For this purpose, equation (27) is multiplied by C_i^m and integrated for the section $[C_{\min}, C_{\max}]$. The result is

$$d\left\langle C_i^m\right\rangle/d\tau = (\Lambda/D)^2\left(B_i + \Lambda^2 D_i\right)\left(C_{\max}^m\,\partial P_1(C_{\max},\tau)/\partial C_i - C_{\min}^m\,\partial P_1(C_{\min},\tau)/\partial C_i\right) -$$

$$-(\Lambda/D)^2\left(B_i + \Lambda^2 D_i\right)\left(mC_{\max}^m P_1(C_{\max},\tau) - mC_{\min}^m P_1(C_{\min},\tau) + m(m-1)\left\langle C_i^{m-2}\right\rangle\right) -$$

$$-C_{\max}^m Q_i^d(C_{\max})P_1(C_{\max},\tau) + C_{\min}^m Q_i^d(C_{\min})P_1(C_{\min},\tau) + m\int_{C_{\min}}^{C_{\max}} C_i^{m-1}P_1(C_i,\tau)Q_i^d(C_i)\,dC_i -$$

$$-C_{\min}^{m+1}P_1(C_{\min},\tau) + C_{\max}^{m+1}P_1(C_{\max},\tau) - 2m\int_{C_{\min}}^{C_{\max}} C_i^m P_1(C_i,\tau)\,dC_i -$$

$$-C_{\max}^m \int_{C_{\min}}^{C_{\max}} P_2(C_i, C_{i-1},\tau)C_{i-1}\,dC_{i-1} + C_{\min}^m \int_{C_{\min}}^{C_{\max}} P_2(C_{\min}, C_{i-1},\tau)C_{i-1}\,dC_{i-1} -$$

$$-C_{\max}^m \int_{C_{\min}}^{C_{\max}} P_2(C_i, C_{i+1},\tau)C_{i+1}\,dC_{i+1} + C_{\min}^m \int_{C_{\min}}^{C_{\max}} P_2(C_{\min}, C_{i+1},\tau)C_{i+1}\,dC_{i+1} -$$

$$+m\int_{C_{\min}}^{C_{\max}} C_i^{m-1}dC_i\int_{C_{\min}}^{C_{\max}} P_1\left(C_i,\mathrm{C}_{i-1},\tau\right)C_{i-1}dC_{i-1}+m\int_{C_{\min}}^{C_{\max}} C_i^{m-1}dC_i\int_{C_{\min}}^{C_{\max}} P_1\left(C_i,\mathrm{C}_{i+1},\tau\right)C_{i+1}dC_{i+1}$$

.

It follows herefrom that, taking account of the above calculated boundary conditions, the result is

$$d\left\langle C_i^m\right\rangle/d\tau=\left(\Lambda/D\right)^2\left(B_i+\Lambda^2D_i\right)m\left(m-1\right)+m\left\langle C_i^{m-1}Q_i^d\left(C_i\right)\right\rangle-2m\left\langle C_i^m\right\rangle+$$
$$+m\left\langle C_i^{m-1}C_{i-1}\right\rangle+m\left\langle C_i^{m-1}C_{i+1}\right\rangle,m=1,2,...,i=2,...,n-1. \quad (45)$$

The result of the similar integration in (28) and (29) is

$$m\left\langle C_1^{m-1}C_2\right\rangle-m\left\langle C_1^m\right\rangle+m\left(m-1\right)\left\langle C_1^{m-2}\right\rangle\left(\left(\Lambda/D\right)^2\left(B_{11}+\beta_1^2B_0\right)/\left(1+\beta_1\Lambda/D\right)\right)-$$
$$-\left(\beta_1\Lambda/D\right)m\left(\left\langle C_1^m\right\rangle-\varphi_1\left(\tau\right)\left\langle C_1^{m-1}\right\rangle\right)=0,m=1,2,... \quad (46)$$

$$m\left\langle C_n^{m-1}C_{n-1}\right\rangle-m\left\langle C_n^m\right\rangle+m\left(m-1\right)\left\langle C_n^{m-2}\right\rangle\left(\left(\Lambda/D\right)^2\left(B_{(n-1)(n-1)}+\beta_2^2B_n\right)/\left(1+\beta_2\Lambda/D\right)\right)-$$
$$-\left(\beta_2\Lambda/D\right)m\left(\left\langle C_n^m\right\rangle-\varphi_2\left(\tau\right)\left\langle C_n^{m-1}\right\rangle\right)=0,m=1,2,... \quad (47)$$

Equations (46) and (47) were derived taking into account that

$$-\int_{C_{\min}}^{C_{\max}} C_j^m\,\partial/\partial C_j\left\langle d\theta_j/d\tau\,\delta\left(C_j-\Theta_j\left(\tau\right)\right)\right\rangle dC_j=d/d\tau\int_{C_{\min}}^{C_{\max}} C_j^m\left\langle\delta\left(C_j-\Theta_j\left(\tau\right)\right)\right\rangle dC_j=$$
$$=d\left\langle C_j^m\right\rangle/d\tau,\ j=1,n,$$

and these summands are canceled with the respective equal summands in the left part of these equations.

4.2. Continual equations for average concentration and concentration dispersion.

Equations (45)–(47) are used to derive the boundary problems in the continual limit for the first two moments of random distribution of diffusant in the diffusion transfer region [12–17]. The derived problems are exposed below.

Assuming that $m=1$ in (45) – (47), we have

$$d\left\langle C_i\right\rangle/d\tau=\left\langle C_i\right\rangle+\left\langle C_{i+1}\right\rangle-2\left\langle C_i\right\rangle+\left\langle Q_i^d\left(C_i\right)\right\rangle,i=2,...,n-1, \quad (48)$$

$$\left\langle C_2\right\rangle-\left\langle C_1\right\rangle-\left(\beta_1\Lambda/D\right)\left(\left\langle C_1\right\rangle-\varphi_1\left(\tau\right)\right)=0, \quad (49)$$

$$\left\langle C_{n-1}\right\rangle-\left\langle C_n\right\rangle-\left(\beta_2\Lambda/D\right)\left(\left\langle C_n\right\rangle-\varphi_2\left(\tau\right)\right)=0. \quad (50)$$

In the continual limit this subtractive problem and the initial condition $\left\langle C\left(x,0\right)\right\rangle=\Phi_0\left(x\right)$ go into the next boundary problem for the diffusion equation (x is the size coordinate x' divided by Λ, $l=L/\Lambda$)

$$\partial\left\langle C\left(x,\tau\right)\right\rangle/\partial\tau=\partial^2\left\langle C\left(x,\tau\right)\right\rangle/\partial x^2+\Lambda^2\left\langle Q\left(x,\tau\right)\right\rangle/D,\ 0<x<l,\tau>0, \quad (51)$$

$$\left\langle C\left(x,0\right)\right\rangle=\Phi_0\left(x\right),\ 0<x<l,\ \tau>0, \quad (52)$$

$$\partial/\partial x\left\langle C\left(0,\tau\right)\right\rangle=\left(\beta_1\Lambda/D\right)\left(\left\langle C\left(0,\tau\right)\right\rangle-\varphi_1\left(\tau\right)\right),\ \tau>0, \quad (53)$$

$$\partial/\partial x\left\langle C\left(l,\tau\right)\right\rangle=-\left(\beta_2\Lambda/D\right)\left(\left\langle C\left(l,\tau\right)\right\rangle-\varphi_2\left(\tau\right)\right),\ \tau>0. \quad (54)$$

Here $\left\langle C\left(x,\tau\right)\right\rangle$ is the average concentration of diffusant in the point x at the time instant τ.

Assuming further that $m=2$ in (45)–(47), we have the following subtractive problem for the second initial moment of the random distribution of diffusant in the diffusion transfer region:

$$d\left\langle C_i^2\right\rangle/d\tau=2\left(\Lambda/D\right)^2\left(B_i+\Lambda^2D_i\right)+2\left\langle C_iQ_i^d\left(C_i\right)\right\rangle+$$
$$+2\left\langle C_iC_{i-1}\right\rangle+2\left\langle C_iC_{i+1}\right\rangle,i=2,...,n-1. \quad (55)$$

$$2\langle C_1C_2\rangle - 2\langle C_1^2\rangle + 2\left(\left(\Lambda/D\right)^2\left(B_{11} + \beta_1^2 B_0\right)/\left(1+\beta_1\Lambda/D\right)\right) - \\ -2\left(\beta_1\Lambda/D\right)\left(\langle C_1^2\rangle - \varphi_1(\tau)\langle C_1\rangle\right) = 0, \quad (56)$$

$$2\langle C_nC_{n-1}\rangle - 2\langle C_n^2\rangle + 2\left(\left(\Lambda/D\right)^2\left(B_{(n-1)(n-1)} + \beta_2^2 B_n\right)/\left(1+\beta_2\Lambda/D\right)\right) - \\ -2\left(\beta_2\Lambda/D\right)\left(\langle C_n^2\rangle - \varphi_2(\tau)\langle C_n\rangle\right) = 0. \quad (57)$$

If to subtract the quantity $d\langle C_i\rangle^2/d\tau$ from the left part of (55) and the equal quantity $2\langle C_i\rangle\left(\langle C_i\rangle + \langle C_{i+1}\rangle - 2\langle C_i\rangle + \langle Q_i^d(C_i)\rangle\right)$ from the right part of (55), the boundary problem obtained in the continual limit from (55)–(57) for the concentration field dispersion $D_c(x,\tau) = \langle C^2(x,\tau)\rangle - \langle C(x,\tau)\rangle^2$ in the point *x* at the instant τ, taking account of the initial condition $D_c(x,0) = D_0(x)$, $B_i = 2\langle C_i\rangle(D/\Lambda)^2/N_V$, (39), and the relation

$2\langle C(x,\tau)\partial^2 C(x,\tau)/\partial x^2\rangle = \partial^2\langle C^2(x,\tau)\rangle/\partial x^2 - 2\left\langle\left(\partial C(x,\tau)/\partial x\right)^2\right\rangle$, will be

$$\partial D_c(x,\tau)/\partial\tau = \partial^2 D_c(x,\tau)/\partial x^2 - 2D_g + 4\langle C(x,\tau)\rangle/N + 2\langle\Lambda^2 C(x,\tau)Q(x,\tau)/D\rangle + \\ +2\left(\Lambda^2/D\right)^2 D_s\left(\langle C(x,\tau)\rangle\right), \quad 0<x<l, \tau>0, \quad (58)$$

$D_c(x,0) = D_0(x)$, $0<x<l$,

$$\partial/\partial x\, D_c(0,\tau) = \left(2\beta_1\Lambda/D\right)D_c(0,\tau) - \frac{1}{\left(1+\beta_1\Lambda/D\right)}\left(\frac{2\langle C(0,\tau)\rangle}{N} + \left(\frac{\beta_1\Lambda\sigma_1(\tau)}{D}\right)^2\right),$$

$\tau > 0$. (59)

$$\partial/\partial x\, D_c(l,\tau) = -\left(2\beta_2\Lambda/D\right)D_c(l,\tau) + \frac{1}{\left(1+\beta_2\Lambda/D\right)}\left(\frac{2\langle C(l,\tau)\rangle}{N} + \left(\frac{\beta_2\Lambda\sigma_2(\tau)}{D}\right)^2\right) \quad (60)$$

where $\tau > 0$, $D_g = \left\langle\left(\partial C(x,\tau)/\partial x\right)^2\right\rangle - \left(\partial\langle C(x,\tau)\rangle/\partial x\right)^2$ is the concentration gradient dispersion negligible in comparison with the summand $\partial^2 D(x,\tau)/\partial x^2$; $D_s\left(\langle C(x,\tau)\rangle\right)$ is the continual representation of D_i according to formula (44), the specific instance of which is considered below.

It follows from the kind of boundary problem for the distribution dispersion of diffusant in the material, like in [8-17], the type of the indicated boundary problem is the same as the type of the boundary problem for the average concentration. When the diffusing substance enters into a reaction with the molecules of the medium (solvent), one can represent the dimensionless diffusant runoff capacity $Q(x,\tau)$ as

$$Q(x,\tau) = -N^2\nu C(x,\tau)\left(1 - C(x,\tau)\right)\exp\left(-U/(kT)\right). \quad (61)$$

Here ν is the frequency (number per unit of time) of attempts to overcome the energy shield of *U (U* is the reaction activation energy) in the line of reaction, k is Boltzmann's constant, *T* is the temperature.

Subsequently, in equation (51) we have

$$\langle Q(x,\tau)\rangle = -N^2\nu\exp\left(-U/(kT)\right)\left(\langle C(x,\tau)\rangle\left(1 - \langle C(x,\tau)\rangle\right) - D_c(x,\tau)\right). \quad (62)$$

Taking account of (52) and (61), the result derived from (44) is

$$D_s\left(\left\langle C(x,\tau)\right\rangle\right)=-\left\langle Q'(x,0)\right\rangle\left(D/\Lambda^2\right)^2\left(\left\langle C^2(x,\tau)\right\rangle+\Phi_0^2(x)+\left(Q(x,0)/Q'(x,0)\right)^2-\right.$$
$$\left.-2\left\langle C(x,\tau)\right\rangle\Phi_0(x)+\left(\left\langle C(x,\tau)\right\rangle-\Phi_0(x)\right)\left(Q(x,0)/Q'(x,0)\right)\right) \qquad (63)$$

$$\left\langle \Lambda^2 C(x,\tau)Q(x,\tau)/D\right\rangle=$$
$$=-\left(\Lambda^2/D\right)N^2\nu\exp\left(-U/(kT)\right)\left(D_c(x,\tau)+\left\langle C(x,\tau)\right\rangle^2-\left\langle C^3(x,\tau)\right\rangle\right). \qquad (64)$$

In the case in question, there are, therefore, two correlated boundary problems for the average diffusant distribution concentration and for its dispersion. These problems are solved both, analytically [19] and numerically [20,21].

4.3. Average concentration and dispersion equations generalized for the 3D case. Boundary problems (51)–(54) and (58)–(60) are recorded in their 3D form as

$$\partial\left\langle C(M,t)\right\rangle/\partial t=D\Delta\left\langle C(M,t)\right\rangle+\left\langle Q(M,t)\right\rangle,\ M\in G, t>0, \qquad (65)$$

$$\left\langle C(M,0)\right\rangle=\Phi_0(M), M\in G, \qquad (66)$$

$$-D\partial/\partial n\left\langle C(M,t)\right\rangle=\beta(M)\left(\left\langle C(M,t)\right\rangle-\varphi(M,t)\right), M\in S, t>0. \qquad (67)$$

$$\partial D_c(M,t)/\partial t=D\Delta D_c(M,t)+4\left(D/\left(N\Lambda^2\right)\right)\left\langle C(M,t)\right\rangle+2\left\langle C(M,t)Q(M,t)\right\rangle+$$
$$+\left\langle Q(M,t)\right\rangle D/\left(2N\Lambda^2\right), M\in G, t>0, \qquad (68)$$

$$-D\partial/\partial n\, D_c(M,t)=2\beta(M)D_c(M,t)-$$
$$-\frac{1}{\left(1+\Lambda\beta(M)/D\right)}\left(\frac{2\left\langle C(M,t)\right\rangle}{N}+\left(\frac{\beta(M)\Lambda\sigma(M,t)}{D}\right)^2\right). \qquad (69)$$

Here G is the diffusion mass transfer region, S is the limit surface of this region. The quantity D_g in (68) is omitted according to the above given remark.

A major subtask in the developed stochastic model of diffusion mass transfer is played is to find the parameter Λ.

This quantity is found on the condition of small fluctuations in concentration. This condition is formulated either as

$$\iiint_G D_{CT}(M)dV \ll \iiint_G \left\langle C_{CT}(M)\right\rangle^2 dV,$$

where $D_{CT}(M)$ is the stationary solution of (68)–(69) on zero boundary conditions, $\left\langle C_{CT}(M)\right\rangle$ is the stationary solution of (65)–(66), or as $D_{\max} \ll \min\left\langle C_{CT}(M)\right\rangle^2 \quad M\in S$, where $D_{\max}$ is the peak value of $D_{CT}(M) \quad M\in G$, and $\min\left\langle C_{CT}(M)\right\rangle^2$ is the lowest squared concentration of the diffusant on the surface limiting the diffusion mass transfer region.

The first condition is fulfilled when Λ meets the following equation

$$\iiint_V D_{CT}(M)dV=\iiint_V \left\langle C_{CT}(M)\right\rangle^2 dV\left(\left(\left|\Delta C_{\max}\right|/\left\langle \bar{C}_{CT}\right\rangle\right)^m+\left\langle C(M)\right\rangle/N\right) \qquad (70)$$

where $\left|\Delta C_{\max}\right|$ is the maximum difference in concentration on the heat conduction region surface, $\left\langle \bar{C}_{CT}\right\rangle$ is the average concentration in the G region, the integer value of m is selected so that $\left(\left|\Delta C_{\max}\right|/\left\langle \bar{C}_{CT}\right\rangle\right) \ll 1$. Equation (70) takes into account that $\Lambda=\sqrt[3]{V}$ must hold at $\Delta C_{\max}=0$.

5. Conclusion

It is seen from the derived boundary problems for the average concentration and concentration dispersion of diffusing substance that these problems are boundary problems of the same type.

The concentration dispersion is caused by the fluctuations in the diffusant concentration in the transfer region, dispersion in the diffusant source or runoff, and diffusing substance concentration in the environment near the boundaries of the mass transfer region, as well as the capacity of the source or runoff.

The dispersion runoff to the transfer region is the diffusant concentration gradient dispersion.

The role of the diffusant concentration fluctuations in the transfer region depends on the physically infinitesimal volume embodied in the system. The choice of this volume is determined by the diffusion pattern in the transfer region.

The results allow calculating not only the average diffusant concentration in the transfer region but also evaluating the deviations in this concentration from the average value, depending on the stochasticity of external factors and stochastic characteristics of diffusant sources or runoff in the diffusant transfer region, which may serve as the basis for optimizing the control of mass transfer in various engineering procedures.

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