
**CERTAIN PROBLEMS WITH THE APPLICATION OF STOCHASTIC
DIFFUSION PROCESSES FOR DESCRIPTION OF CHEMICAL
ENGINEERING PHENOMENA; KOLMOGOROV AND CLASSIC
DIFFUSION EQUATIONS**

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The paper presents alternative forms of partial differential equations of the parabolic type used in chemical engineering for description of heat and mass transfer. It points at the substantial difference between the classic form of the equations, following from the differential balances of mass and enthalpy, and the form following from the concept of stochastic motion of particles of mass or energy component. Examples are presented of the processes that may be described by the latter method. The paper also reviews the cases when the two approaches become identical.

Mathematical theory of diffusion processes, i.e. random processes continuous with respect to time and spatial coordinates (see e.g. refs^{1,2}) is successfully applied in various parts of natural sciences^{1,3,4}. In chemical engineering this approach has been used for instance in description of processes in solid-liquid systems⁵⁻⁹, gas-liquid systems^{6,10}, dispergation and coalescence of immiscible liquids^{11,12}, dispergation¹³ and blending¹⁴ of solids. Another region is the application of these processes to continuous mixers¹⁵⁻¹⁸ and reactors¹⁹⁻²³. Certain results, together with the explanation of the mathematical apparatus, have been treated in chemical engineering monographs^{24,25}.

Partial differential equations, generally used in chemical engineering for description of mass and energy transfer (see e.g. refs^{26,27}), belong, from the standpoint of terminology of random processes, into the class of so-called diffusion equations, often referred to as the Kolmogorov or Fokker-Planck equations (see e.g. refs²⁻⁴). In any case, the attempts for a mathematical description of the Brownian motion and the concept of the mechanism of molecular motion just led to elaboration of the above-mentioned mathematical apparatus (see e.g. the introductory chapter of the work of Ito and McKean²⁸).

It turns out, however, that in the general case the classic form of the transport equations and the Kolmogorov diffusional equations is not identical as there are differences in the notation of the diffusion terms. In order to express this disagreement

as clearly as possible, let us write first the differential mass balance of a component and the enthalpy balance with some simplifications. The Kolmogorov equation and the relationships leading to it shall be consistently treated as relations permitting description of the probability characteristic of the kinematics of motion of a single particle of the component considered in the three-dimensional Euclid space.

THEORETICAL

Formulation of the Mass and Enthalpy Balance

We shall consider separately the transport of the mass component and heat in the moving and incompressible fluid, i.e. we shall consider the temperature or concentration changes have no significant effect on the density of the fluid (or on the density of the fluid and the diffusing component). In both equations there will be no source terms either. In the mass balance we shall consider an isothermal process, neglect the effect of external forces, thermodiffusion and pressure gradients. In the energy balance we shall consider as insignificant the terms describing changes of kinetic and potential energy of the fluid compared to the changes of its enthalpy. Apart from that we shall consider that the specific heat capacity of the fluid does not significantly depend on its temperature.

Based on the summarized assumptions one can write the differential balance of the component A in the form (see e.g. refs^{26,27})

$$\partial \varrho_A / \partial t + \nabla \cdot (\mathbf{v} \varrho_A) + \nabla \cdot \mathbf{j}_A = 0, \quad (1)$$

where ϱ_A designates partial density of the mass component, t is time and \mathbf{v} is the velocity of the fluid which is generally a vector function of time and spatial coordinates; it is assumed that this is a known function. The symbol ∇ designates the Hamilton differential operator in the Euclid three-dimensional space and \mathbf{j}_A is a diffusional flux determined by the first Fickian law

$$\mathbf{j}_A = -D \nabla \varrho_A. \quad (2)$$

The diffusivity is generally regarded to be a known scalar function of time, spatial coordinates and the concentration of component A. The diffusional flux characterises the relative motion of the component in the mixture; the sum of the fluxes of all components making up the considered fluid must therefore vanish. The sum of partial densities of all components equals the density of the incompressible fluid; summation of Eq. (1) over all components yields the familiar relationship

$$\sum_A \left[\frac{\partial \varrho_A}{\partial t} + \nabla \cdot (\mathbf{v} \varrho_A) + \nabla \cdot \mathbf{j}_A \right] = \frac{\partial \varrho}{\partial t} + \nabla \cdot (\mathbf{v} \varrho) = \nabla \cdot \mathbf{v} = 0, \quad (3)$$

stating that the divergence of the velocity of an incompressible fluid equals zero.

Upon considering Eqs (2) and (3) the differential mass balance in the "classic" form reads

$$\partial \varrho_A / \partial t + \mathbf{v} \cdot \nabla \varrho_A - \nabla \cdot (D \nabla \varrho_A) = 0; \quad (4)$$

partial density $\varrho_A = \varrho_A(\mathbf{x}, t)$ is the solution of this equation for the given initial and boundary conditions.

Analogously one can write the differential enthalpy balance

$$\partial(\varrho c_p T) / \partial t + \nabla \cdot (\mathbf{v} \varrho c_p T) + \nabla \cdot \mathbf{q} = 0, \quad (5)$$

where T designates temperature, c_p is the specific heat capacity of the fluid and \mathbf{q} is the heat flux determined by the Fourier law

$$\mathbf{q} = -\lambda \nabla T \quad (6)$$

while the thermal conductivity is generally taken to be a scalar function of coordinates, time and temperature. After substituting from Eqs (6) and (3) into Eq. (5) and upon considering the assumption of constant density and heat capacity one obtains the „classic" equation for the transport of heat

$$\partial T / \partial t + \mathbf{v} \cdot \nabla T - \nabla \cdot (a \nabla T) = 0, \quad (7)$$

where $a = \lambda / \varrho c_p$ is the thermal diffusivity. Solution of the equation $T = T(\mathbf{x}, t)$ is the temperature of an incompressible fluid.

Equations (4) and (7) have been used for description of heat and mass transfer in a turbulent incompressible fluid (see e.g. ref.²⁹); its velocity in this case is taken to be a random vector function of time and spatial coordinates. From here it follows that also the solution of these equations – the partial density of the component or temperature – become also random scalar functions of these arguments.

The most frequent modification of Eq. (4) is then the method of averaging, i.e. calculation of expected values, of individual quantities appearing in this equation, i.e.

$$\partial \langle \varrho_A \rangle / \partial t + \langle \mathbf{v} \rangle \cdot \nabla \langle \varrho_A \rangle + \nabla \cdot (\langle \mathbf{v}' \varrho_A \rangle) - \nabla \cdot (D \nabla \langle \varrho_A \rangle) = 0, \quad (8)$$

where the brackets indicate mean values; the apostrophes the fluctuations of the corresponding quantities around their means, i.e. for instance

$$\varrho_A(\mathbf{x}, t) = \langle \varrho_A(\mathbf{x}, t) \rangle + \varrho'_A(\mathbf{x}, t). \quad (9)$$

Mutual correlation of random velocity and the concentration of the component is usually taken proportional to the gradient of the mean concentration²⁹.

$$\langle \mathbf{v}' \varrho'_A \rangle = -\mathbf{D}_T(\mathbf{x}, t) \cdot \nabla \langle \varrho_A \rangle, \quad (10)$$

where the coefficient of proportionality \mathbf{D}_T —generally a function of spatial coordinates and time — is usually termed turbulent diffusivity and is generally a second order tensor. Superposition of molecular and turbulent diffusivity $\mathbf{D} = \mathbf{D}_T + \mathbf{D}$ permits finally Eq. (8) to be written in the form

$$\partial \langle \varrho_A \rangle / \partial t + \langle \mathbf{v} \rangle \cdot \nabla \langle \varrho_A \rangle - \nabla \cdot (\mathbf{D} \cdot \nabla \langle \varrho_A \rangle) = 0. \quad (11)$$

The coefficient \mathbf{D} shall be termed the tensor of diffusion and shall be regarded as a symmetric one.

An analogous procedure yields the relationship for the transport of heat in the turbulent medium.

$$\partial \langle T \rangle / \partial t + \langle \mathbf{v} \rangle \cdot \nabla \langle T \rangle - \nabla \cdot (\mathbf{A} \cdot \nabla \langle T \rangle) = 0, \quad (12)$$

where \mathbf{A} shall be regarded as a symmetric tensor of temperature diffusivity. In the following text we shall omit brackets designating the averaging procedure.

The Kolmogorov Diffusion Equation

We shall present now the method applicated in the theory of random processes to derive the relationship of analogous type. Let us consider now that an elementary particle (molecule) of the component A moves at random in a fluid and its motion is given by the position vector $\mathbf{X}(t)$, the latter being a random function of time. Let us assume that for this process there exists a transition probability density in the form

$$f(\mathbf{x}; t | \mathbf{y}; \tau) = \frac{\partial^3}{\partial x_1 \partial x_2 \partial x_3} P\{X_1(t) \leq x_1; X_2(t) \leq x_2; X_3(t) \leq x_3 | \mathbf{X}(\tau) = \mathbf{y}\}, \quad (13)$$

where $t > \tau$ and $x_i (i = 1, 2, 3)$ are the coordinates of the vector \mathbf{x} . This function characterises the probability of the position of a molecule A at the time instant t under the condition that in some of the preceding instant τ the molecule was at the point determined by the position vector \mathbf{y} .

If the process under consideration is a Markov one, i.e. such that it depends on the initial conditions only and not on the transient states, one can write the Chapman-Kolmogorov equation (see e.g. refs^{2,4})

$$f(\mathbf{x}; t|\mathbf{y}; \tau) = \int f(\mathbf{x}; t|\mathbf{z}; s)f(\mathbf{z}; s|\mathbf{y}; \tau) d\mathbf{z} \quad [t > s > \tau], \quad (14)$$

excluding the effect of the position of the particle at the transient state s on the probability of its localisation at the instant t .

For a diffusional Markov process there exists another condition determining the continuity of the process

$$\lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{|\mathbf{x}-\mathbf{y}| > \epsilon} f(\mathbf{x}; t + \Delta t|\mathbf{y}; t) d\mathbf{x} = 0, \quad (15)$$

i.e. in this case the trajectory of the molecule of the component and further expressions for the first two infinitesimal moments of the process

$$\mathbf{a}(\mathbf{y}, t) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{|\mathbf{y}-\mathbf{x}| \leq \epsilon} (\mathbf{x} - \mathbf{y}) f(\mathbf{x}; t + \Delta t|\mathbf{y}; t) d\mathbf{x} \quad (16)$$

$$\mathbf{B}(\mathbf{y}, t) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{|\mathbf{y}-\mathbf{x}| \leq \epsilon} (\mathbf{x} - \mathbf{y})^2 f(\mathbf{x}; t + \Delta t|\mathbf{y}; t) d\mathbf{x}, \quad (17)$$

while the vector \mathbf{a} is usually termed the drift velocity; the matrix of the second order tensor \mathbf{B} the diffusion matrix. From the definition it follows that this matrix is symmetric and positively definite.

From the validity of Eqs (14)–(17) there follows (see e.g. refs^{2,4}) the Kolmogorov forward diffusion equation (in physical applications usually termed the Fokker-Planck equation)

$$\partial f / \partial t + \nabla \cdot (\mathbf{a}f) - 1/2 \nabla \cdot (\mathbf{B}f) = 0. \quad (18)$$

In the literature unusual sequence of differential operators has been made possible here by the fact that the motion of the particle takes place in the three-dimensional Euclid space and that the tensor \mathbf{B} is symmetric.

In view of the fact that Eq. (18) is linear with respect to the function $f(\mathbf{x}; t|\mathbf{y}; \tau)$, an unconditional probability density $p(\mathbf{x}; t)$ is another solution of this equation for given initial probability density $p(\mathbf{y}; 0)$

$$p(\mathbf{x}; t) = \int f(\mathbf{x}; t|\mathbf{y}; 0) p(\mathbf{y}; 0) d\mathbf{y}. \quad (19)$$

A Comparison of the Classic Transport Equations with the Kolmogorov Equation

In order to simplify the situation we shall assume in this paragraph that the processes under consideration take place in a bounded part of the three-dimensional space; the boundaries of this subspace are isolated with respect to mass and energy transfer. Further we compare individual terms in Eq. (18), considering also Eq. (19), and in Eqs (11) and (12); the relationship between them shall be written in the form of the following postulates:

1. The probability density $p(\mathbf{x}; t)$, characterising the position of an individual molecule of the component A is directly proportional to the partial density of this component; the coefficient of proportionality is the total mass of component A in the isolated subspace under consideration.

$$\varrho_A(\mathbf{x}, t) = M_A p(\mathbf{x}; t) = N_A m_A p(\mathbf{x}; t), \quad (20)$$

where N_A designates the total number of particles of component A and m_A the mass of each of them. The above relationship holds the better the greater is the number of particles of the component A occupying the subspace considered, as follows from one of the oldest axioms of the classic theory of probability – the Bernoulli law of the large numbers.

Upon taking for the elementary event the fact that a single particle of the component A appears at a time instant t in a very small subspace of volume ΔV with the center at the point \mathbf{x} , then we may write for every $\varepsilon > 0$, (see e.g. ref.³⁰) the relationship

$$\lim_{N_A \rightarrow \infty} P \left\{ \left| \frac{n_A(t, \Delta V)}{N_A} - \int_{\Delta V} p(\mathbf{x}; t) d\mathbf{x} \right| \geq \varepsilon \right\} \rightarrow 0, \quad (21)$$

where n_A designates the number of occurrences of event as the number of mutually independently moving particles of the component satisfying the condition of the elementary event. The written difference converges to zero with the increasing number of particles. Upon multiplying both terms of the difference by the overall mass M_A and upon dividing by a very small value ΔV one obtains Eq. (20). A similar relationship is valid for the expected value of the concentration of the component.

It has to be noted through that the concentration of the component cannot be too high in order to fulfill the requirement of independence of the events. This condition may be interpreted also in such a way that the motion of individual particles of the component is conditioned only by the motion of the liquid that carries it and that mutual interactions between particles of the component A are unlikely.

2. The drift velocity of particles of the component A equals the velocity of the fluid, or, in a turbulent medium, equals the expected value of this velocity.

$$\mathbf{a}(\mathbf{x}, t) = \mathbf{v}(\mathbf{x}, t) = \langle \mathbf{v}(\mathbf{x}, t) \rangle. \quad (22)$$

The drift velocity, according to the definition (16), is the ratio of the expected value of the infinitesimal shift of the particle and the infinitesimal time interval. It is assumed at the same time that we may neglect the effect of external forces acting on the particle as well as the effect of inertia forces. On the basis of considerations analogous to those in the preceding paragraph we may state that for the description of the particle a kinematic concept will suffice and that the averaged motion of the particle is solely determined by the motion of the liquid surrounding the particle.

3. The physical meaning of the tensor \mathbf{B} in Eq. (17) considered for a large amount of particles of the component A is identical with the physical meaning of the diffusion tensor in Eq. (11). Tensor \mathbf{B} characterises intensity with which the variance of the position vector alters, i.e. for a large number of particles the intensity of their scatter in the fluid that carries them. From the formulation of the axiom it does not follow that in the general case the following identity is valid

$$\mathbf{D}(\mathbf{x}, t) = \mathbf{B}(\mathbf{x}, t)/2. \quad (23)$$

Conditions under which this is possible shall be subject to the following considerations. Apart from that it is obvious that this function, characterising the relative motion of the component A in the fluid, is conditioned e.g. by the form of the particles of this component and the fluid. The form of the function \mathbf{D} or \mathbf{B} is therefore generally different for different species.

4. The probability density $p(\mathbf{x}, t)$ is directly proportional to the enthalpy of the fluid at the point \mathbf{x} and the time instant t ; the coefficient of proportionality is the overall enthalpy H in the isolated subspace.

$$c_p \rho T(\mathbf{x}, t) = H p(\mathbf{x}, t). \quad (24)$$

Under the above assumptions regarding the independence of the density and the specific heat capacity of the fluid on the temperature we may write that also the temperature is directly proportional to the probability density $p(\mathbf{x}; t)$. While, however, the random vector $\mathbf{X}(t)$ in the formulation of the first postulate has clearly the meaning of the instantaneous position of the mass particle in space, it is necessary in this case to consider a random motion of a certain amount of energy, on the one hand, carried by individual particles, and, on the other hand, exchanged among the particles.

5. The drift velocity of this energy quantum equals the velocity of the fluid or its expected value. Equation (22) therefore also holds.

6. Tensor \mathbf{B} in Eq. (17) is analogous to the tensor of thermal diffusivity \mathbf{A} in Eq. (12). On the basis of the considerations in point 3 it is apparent that the form of the function \mathbf{A} depends generally on the properties of the flowing fluid. Here again the following identity is generally not valid

$$\mathbf{A}(\mathbf{x}, t) = \mathbf{B}(\mathbf{x}, t)/2. \quad (25)$$

In the following paragraph we shall first discuss the differences between these tensors and also between tensors \mathbf{D} and \mathbf{B} .

The Differences in Diffusional Terms of Differential Equations

From the considerations and relationships in the previous paragraph it follows that Eq. (18) is first integrated as in Eq. (19) and multiplied by the constant M_A ; thus we obtain, considering still Eq. (22), the following

$$\partial \varrho_A / \partial t + \nabla \cdot (\mathbf{a} \varrho_A) - 1/2 \nabla \cdot (\nabla \cdot (\mathbf{B} \varrho_A)) = 0 \quad (26)$$

Kolmogorov differential equation for the partial density of the component A. Upon multiplying by the constant $H/c_p \varrho$ one obtains an analogous relationship for the temperature of the fluid as

$$\partial T / \partial t + \nabla \cdot (\mathbf{a} T) - 1/2 \nabla \cdot (\nabla \cdot (\mathbf{B} T)) = 0. \quad (27)$$

A comparison of these two relationships with Eqs (11) and (12) shows the difference in the notation of the second (convective) and the third (diffusion) term.

It is apparent that the expressions $\nabla \cdot (\mathbf{a} \varrho_A)$ and $\nabla \cdot (\mathbf{a} T)$ correspond to analogous expressions for a compressible fluid (see e.g. ref.²⁷) and in this more general case thus the second terms of all mentioned equations are identical. From the standpoint of the description of convective transport of mass and energy thus there is not a difference between the Kolmogorov and the differential balances.

The condition $\nabla \cdot \mathbf{a} = 0$ in Eqs (26) and (27) apparently poses additional limitations on the form of the function f in Eqs (15)–(17). This condition is fulfilled, for instance, if the function f is invariant with respect to the shift. We shall now examine differences in the last (i.e. diffusional) terms of these equations.

Primarily it is the difference in the location of the differential operator; in the Kolmogorov equation elements of the diffusional matrix are differentiated twice. Apart from that the formulation of the differential balances does not rule out the dependence of the diffusion tensor on the concentration of the component and the

tensor of thermal diffusivity on the temperature (see e.g. ref.²⁷).

$$\mathbf{D} = \mathbf{D}(\mathbf{x}, t, \varrho_A(\mathbf{x}, t)); \quad \mathbf{A} = \mathbf{A}(\mathbf{x}, t, T(\mathbf{x}, t)). \quad (28)$$

The balances equations thus become nonlinear in contrast to the Kolmogorov equation (18), which — as follows from the derivation (see e.g. ref.⁴) — is always linear with respect to the probability density.

In the general case thus the compared pairs of equations (11) and (26) and further (12) and (27) are not identical and cannot describe the identical process. Their applicability apparently depends on the fact how accurately the particular equation is capable of expressing the real process. In chemical engineering the preference in general is given to the differential balances as they can (in contrast to the Kolmogorov equation) express also the well known fact that at steady state the temperature and concentration in an isolated system are constants.

There exist, however, in chemical engineering also certain processes which, on the contrary, can be successfully described provided that the diffusional terms are written in the form given in Eqs (26) or (27). King¹⁷, for instance, introduced into the chemical engineering literature the following formulation of the Kolmogorov equation

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial x} [(\beta + \gamma - \alpha x) p] - \frac{\partial^2}{\partial x^2} (\gamma x p) = 0, \quad (29)$$

where α , β , and γ are constants. Solution of this equation in the steady state is the probability density, the so-called gamma-distribution, which is used for description of the distribution of the residence time of the fluid in the continuous flow equipment³¹. This description was successfully used also for modelling of an industrial equipment — the flocculation chamber³².

The two-dimensional Kolmogorov equation with the scalar diffusion coefficient as a function of position permitted one to express the existence of the local extremes of the concentration of solids that had been experimentally found in a batch mixed by a mechanical rotational impeller. Use of the “classic” differential balance did not permit description of these extremes⁸.

A very illustrative example in this sense is the description of the function of the horizontal drum mixer for blending solid particles. Mixing of particles of the same size differing in color leads to their axial mixing in accord with the one dimensional diffusion equation^{33,34} $\partial c/\partial t = D\partial^2 c/\partial x^2$, in which the diffusion coefficient is a constant and c designates concentration of one of the color components. In case, however, that the particle differ as to their dimensions, one can observe, in contrast, their axial (and eventually also radial) segregation. As noted by Fan and Shin¹⁴, this experimental observation can be in principle described by the Kolmogorov

equation in the form $\partial c/\partial t = \partial^2(D(x)c)/\partial x^2$. The classic balance $\partial c/\partial t = \partial(D(x)\partial c)/\partial x^2$ in this case fails as it leads to equalization of concentration of particles of one dimension. The proposed application of the Kolmogorov equation was successfully realized³⁵ for interpretation of experimental data³⁶.

The classic formulation of the differential equations (11) and (12) thus cannot be in all cases preferred and the chemical engineering monographs and textbooks dealing with the study of mass and energy balances in general terms should also deal with alternative methods of formulation of diffusion equation (26) and (27).

In the general case these two approaches cannot be unified and in ambiguous cases one has to consider, or eventually experimentally verify, the suitability of the particular expression. In the following paragraph we shall attempt to review the cases when it is possible to transform one expression to the other which eliminates the necessity of choosing between them.

The Cases of Possible Unification of the Two Types of Equations

The "non-linear" form of the Kolmogorov equation. The method outlined in one of the preceding paragraphs led to the Kolmogorov equation (18) which represents a linear relationship with respect to the probability density. The diffusion tensor \mathbf{B} in this equation thus cannot be written in the form analogous to Eqs (28). In this paragraph we shall attempt to outline the concept which would nevertheless lead to the diffusion tensor as an explicit function of the probability density.

In the previous paragraph we have considered that the motion of particles of the component A is such that mutual interaction is negligible. Now we shall assume that at higher concentrations of the component A this concept no longer holds. Let us admit though that even this higher concentration does not affect significantly the flow of the incompressible fluid. Further we shall confine this problem by the assumption usual in the statistical mechanics that mutual interactions of the particles may be approximated by summation of the interactions between pairs of particles and that these interactions are symmetric (see e.g. ref.³⁷).

We shall therefore write the Kolmogorov forward equation for simultaneous motion of a pair of molecules of the component A, designated i and j

$$\begin{aligned} \frac{\partial f_2}{\partial t} + \nabla_i \cdot (\mathbf{a}(\mathbf{x}_i, t) f_2) + \nabla_j \cdot (\mathbf{a}(\mathbf{x}_j, t) f_2) - 1/2 \nabla_i \cdot (\nabla_i \cdot \mathbf{B}_2(\mathbf{x}_i, \mathbf{x}_j, t) f_2) - \\ - 1/2 \nabla_i \cdot (\nabla_j \cdot \mathbf{C}(\mathbf{x}_i, \mathbf{x}_j, t) f_2) - 1/2 \nabla_j \cdot (\nabla_i \cdot \mathbf{C}^T(\mathbf{x}_i, \mathbf{x}_j, t) f_2) - \\ - 1/2 \nabla_j \cdot (\nabla_j \cdot \mathbf{B}_2(\mathbf{x}_j, \mathbf{x}_i, t) f_2) = 0, \end{aligned} \quad (30)$$

where ∇_i and ∇_j designate differential operators with respect to position coordinates of particles i and j. Physical concept of the velocity of fluid unaffected by the con-

centration of the component A can be here reformulated in the sense that the velocity of the drift is given by summation of identical vector functions of position of individual particles, or, explicitly, also time. The diffusion terms express interactions between particles respecting their symmetry.

The solution is the "double" conditional probability density f_2 for the position of both particles at the time instant t , for their given initial positions and may be defined analogously as the function f in Eq. (13). Similarly as in Eq. (19) one can also find an unconditional probability density characterising simultaneous positions of particles i and j :

$$p_2(\mathbf{x}_i, \mathbf{x}_j; t) = \iint f_2(\mathbf{x}_i, \mathbf{x}_j; t | \mathbf{y}_i, \mathbf{y}_j; 0) p_2(\mathbf{y}_i, \mathbf{y}_j) d\mathbf{y}_i d\mathbf{y}_j. \quad (31)$$

Finally integration with respect to the instantaneous position of one of the particles leads to the probability density function for the second particle, that is for instance to

$$p_1(\mathbf{x}_i; t) = \int p_2(\mathbf{x}_i, \mathbf{x}_j; t) d\mathbf{x}_j. \quad (32)$$

It is apparent that in view of the symmetry considered the probability density for the other of the particles shall be identical. It is further obvious that this function is identical with the function p in Eq. (19) only provided that the particles move independently.

The last function is a solution of Eq. (30) after integrations indicated in Eqs (31) and (32). At the same time it is assumed that the sequence of the integration and derivation can be interchanged and that the coefficients in the equations are of such a form that the last three terms assume after these operations a zero value:

$$\partial p_1 / \partial t + \nabla \cdot (\mathbf{a}(\mathbf{x}_i, t) p_1) - 1/2 \nabla_i \cdot \nabla_i \cdot \{ [\int \mathbf{B}_2(\mathbf{x}_i, \mathbf{x}_j, t) p_2 d\mathbf{x}_j / p_1] p_1 \} = 0. \quad (33)$$

The expression in the brackets may be regarded to be the definition of the diffusion tensor for the motion of a single particle which, however, characterises also the effect of interactions on part of the second particle. It is, however, apparent that with this approach the coefficient of diffusion is generally only a function of time and position vector \mathbf{x}_i . According to the above considerations the net interaction would be expressed by the summation of all diffusion coefficients characterising the effect of other particles on the i -th particle.

A particular case leading to an explicit dependence of the diffusion tensor on the probability density p_1 may be formulated on the following assumptions: 1) The diffusion coefficient characterising the interaction is a function of the distance between both particles and independent of the position of the latter. 2) This dependence is a deterministic function of the probability density characterising position of the particle under consideration.

The introduced assumptions are very stringent and may be approximately fulfilled only if we consider the interaction between particles to be significant only within a limited distance between them (narrow potential "pit" expressed, for instance, by the Lennard-Jones potential³⁷). This distance decreases with the increased number of particles of the component A in the mixture.

The expression in the bracket in the last term of Eq. (33) could be, under these assumptions, written in the following form

$$\begin{aligned} & \int \mathbf{B}_2(\mathbf{x}_i, \mathbf{x}_j, t) p_2(\mathbf{x}_i, \mathbf{x}_j; t) d\mathbf{x}_j / p_1(\mathbf{x}_i; t) = \\ & = \int \mathbf{B}_r(|\mathbf{r}|, \mathbf{x}_i, t) p_2(\mathbf{x}_i, \mathbf{x}_i + \mathbf{r}; t) d\mathbf{r} / p_1(\mathbf{x}_i; t) \quad [\mathbf{r} \equiv \mathbf{x}_j - \mathbf{x}_i]. \end{aligned} \quad (34)$$

In the first coefficient \mathbf{B}_r of the expression behind the integral we have used the first of the assumptions. The vector \mathbf{r} characterises the oriented distance between particles i and j , symbol $|\mathbf{r}|$ denotes its magnitude. The components of the vector \mathbf{r} may be further expressed by means of spherical coordinates (see e.g. ref.³⁸) and the expression may be integrated with respect to two angular coordinates. (The coefficient \mathbf{B}_r is not a function of these coordinates). After this operation the right hand side of Eq. (34) changes to

$$4 \int \mathbf{B}_r(r, \mathbf{x}_i, t) p_r(r, \mathbf{x}_i; t) r^2 dr / p_1(\mathbf{x}_i; t). \quad (35)$$

The ratio $r^2 p_r / p_1$ expresses the conditional probability density characterising the distance between the i -th and the j -th particle under the condition that the former appears at the point \mathbf{x}_i . According to the second of the introduced assumptions this function may be approximately expressed by $r^2 p_r / p_1 \approx \delta_r(r - \Psi(p_1))$, where δ_r is the Dirac function. In view of the dimensionality of the probability density the Ψ function may be further approximated by $\Psi(p_1) \sim p_1^{-1/3}$. Upon substituting these expressions into Eq. (35) and integration one finally obtains an expression for the diffusion coefficient which is an explicit function of the probability density p_1 . The diffusion tensor \mathbf{B}_r thus has in this case a form analogous to the expressions (28). From the above considerations it further follows that for greater distances between particles and hence for lower densities of the probability p_1 (or for lower concentrations of particles) this dependence vanishes and the tensor takes the form written in Eq. (17).

Cases of Identity of Diffusion Coefficients. In this paragraph we shall review the cases when the diffusion coefficients — scalars or tensors — may be written in the differential balances and the Kolmogorov equation in such a way as to achieve the same position of the differential operators in these terms. Let us note first that from this standpoint it is not important whether the diffusion coefficients are explicit functions of time; for simplicity we shall consider that these coefficients are time

independent, i.e. we deal with a diffusion homogeneous in time. As far as the dependence on the spatial coordinates is concerned we shall distinguish these cases:

1. Homogeneous and isotropic diffusion. It is the simplest and in chemical engineering most often used way of describing mass and heat transfer. This is the case when the diffusion coefficient is a scalar constant which may be taken in front of the differentiation sign in Eqs (11), (12), (26), and (27) so that all relations are identical. In the monographs dealing with random Markov processes (see e.g. ref.¹) this case is presented as an example of the agreement of results of the theory of random diffusion processes with transport equations.

2. Homogeneous and anisotropic diffusion. In this case the diffusivity, or the thermal diffusivity, are second order tensors while individual components of the tensor are constants. In the expressions mentioned in the preceding paragraph one may also take these coefficients in front of the differential operators so that for instance Eq. (12) and (27) may be written in the form

$$\partial T / \partial t + \mathbf{v} \cdot \nabla T - \mathbf{A} : \nabla^2 T = 0, \quad (36)$$

where the colon designates the double scalar product and ∇^2 designates the dyadic product of two differential operators.

Expressions of this type have been used in chemical engineering applications for description of heat conduction in solid anisotropic media (see e.g. ref.³⁹) where, of course, the velocity \mathbf{v} equals zero.

3. Inhomogeneous isotropic diffusion. The diffusion coefficient is a scalar, yet a function of spatial coordinates (i.e. for instance $\mathbf{D}(\mathbf{x}) = ID(\mathbf{x})$). In this case Eqs (11), (12), (26), and (27) cannot be generally transformed to a unified form. The literature^{3,24} usually presents an approach based on the derivation of the diffusion term and assigning the "excess" expression to the convective term:

$$\partial \varrho_A / \partial t + \nabla \cdot (\mathbf{v} \varrho_A) - \nabla \cdot ((\nabla D(x)) \varrho_A) - \nabla(D(x)) \cdot \nabla \varrho_A = 0. \quad (37)$$

The third term is called "spurious flow". However, as long as the velocity of the drift is identified with the velocity of the fluid this operation does not usually help. It leads, for instance, to a nonuniform steady state spatial distribution of concentration or temperature which is immediately apparent in the case of a quiescent fluid.

One can, however, point at a class of processes where a similar approach is successful. It is in cases when the diffusion coefficient is only a function of concentration, or the thermal diffusivity only a function of temperature and thus only an implicit function of position and time:

$$\mathbf{D}(\mathbf{x}, t, \varrho_A(\mathbf{x}, t)) = ID(\varrho_A(\mathbf{x}, t)). \quad (38)$$

Using the rules for differentiation of composed functions we obtain $\nabla D(\varrho_A(\mathbf{x}, t)) = (\partial D/\partial \varrho_A) \nabla \varrho_A$ which modifies Eq. (37) to the following form

$$\partial \varrho_A / \partial t + \nabla \cdot (\mathbf{v} \varrho_A) - \nabla \cdot ((\varrho_A \partial D / \partial \varrho_A + D) \nabla \varrho_A) = 0. \quad (39)$$

For the enthalpy balance we may write analogously

$$\partial T / \partial t + \nabla \cdot (\mathbf{v} T) - \nabla \cdot ((T \partial a / \partial T + a) \nabla T) = 0. \quad (40)$$

Expressions in the inner parentheses of the third terms of both equations may be regarded as "corrected" diffusivity or thermal diffusivity.

Both these cases are frequently used in the chemical engineering practice^{39,40}, while we have at our disposal — primarily for the coefficient of thermal diffusivity — extensive amount of experimental data.

4. Inhomogeneous and anisotropic diffusion. The diffusion coefficient is a second order tensor and individual elements of its matrices are functions of spatial coordinates $\mathbf{D} = \mathbf{D}(\mathbf{x})$. Transition to the "clasic" form can be realized as in the previous case, i.e. when the diffusion tensor is a function of the concentration of the component only or if the tensor of thermal diffusivity is a function of temperature only $\mathbf{D} = \mathbf{D}(\varrho_A)$; $\mathbf{A} = \mathbf{A}(T)$.

In this case, however, one can point at another possibility which is, in a way, analogous to the statement of zero divergence of the velocity in an incompressible fluid. In case of a uniform scatter of the component A in the incompressible fluid its partial density is a constant. In order to satisfy this condition we must have $\nabla \cdot \nabla \cdot \mathbf{D} = 0$, i.e. the double divergence of the tensor of diffusion must vanish. A more stringent requirement may be the condition of zero divergence of the tensor $\nabla \cdot \mathbf{D} = \mathbf{0}$, i.e. a vector whose components all vanish. Analogous consideration apparently holds also for the tensor of thermal diffusivity. This approach, however, is not being applied in the chemical engineering applications.

CONCLUSIONS

From the considerations, assumptions and relationships written in this paper one can draw the following conclusions:

1. A random process has been described, represented by the position vector of a particle moving in a three-dimensional Euclid space. Assuming this point to be a diffusional Markov process corresponding Kolmogorov forward differential equation, Eq. (18), has been written, whose solution is the probability density characterising the process.

2. Assumptions have been summarised under which individual terms in this equation may be identified with the expressions appearing in the differential balance

of mass component (Eq. (4)) or enthalpy (Eq. (7)) in the same space. Namely: *a*) the proportionality between the above considered probability density and the partial density of the mass component and the proportionality between the same probability density and temperature, *b*) the identity between the drift velocity and the velocity of the fluid in the balance equations.

3. Under these assumptions in the general case the diffusion terms in the Kolmogorov equation and the differential balances differ. It is so when the diffusion coefficients are functions of spatial coordinates. It has been pointed at the fact that certain chemical engineering processes exist leading to a nonuniform distribution of the concentration of the component. In these cases the classic diffusion equation fails and one has to resort to a more general notation of the diffusion term, given e.g. in Eq. (18).

4. It has been shown that for a large class of chemical engineering processes, when the diffusion coefficient depends on concentration of the component (or the coefficient of thermal conductivity on temperature) and hence it is only an implicit function of spatial coordinates, the diffusion coefficient in Eq. (18) may be transformed to a form corresponding to analogous expressions in Eqs (4) and (7).

LIST OF SYMBOLS

A	tensor of thermal diffusivity, $\text{m}^2 \text{s}^{-1}$
<i>a</i>	thermal diffusivity, $\text{m}^2 \text{s}^{-1}$
a	drift velocity, m s^{-1}
B	diffusion tensor, $\text{m}^2 \text{s}^{-1}$
C	tensor characterizing interparticle interactions, $\text{m}^2 \text{s}^{-1}$
<i>c</i>	concentration of particles
<i>c_p</i>	specific heat of fluid, $\text{J kg}^{-1} \text{K}^{-1}$
<i>D</i>	diffusivity, $\text{m}^2 \text{s}^{-1}$
D	diffusivity (tensor), $\text{m}^2 \text{s}^{-1}$
<i>f</i>	conditional probability density, m^{-3}
<i>f₂</i>	"double" conditional probability density, m^{-6}
<i>H</i>	total enthalpy of fluid, J
I	identity tensor
<i>j</i>	diffusional flux, $\text{kg m}^{-2} \text{s}^{-1}$
<i>M_A</i>	total mass of component A, kg
<i>m_A</i>	mass of particle of component A, kg
<i>N_A</i>	total number of particles of component A
<i>p</i>	probability density (unconditional), m^{-3}
<i>p₂</i>	"double" unconditional probability density, m^{-6}
q	heat flux, W m^{-2}
<i>r</i>	oriented distance between particles, m
<i>T</i>	temperature, K
<i>t</i>	time, s
v	velocity of fluid, m s^{-1}
X	position vector (random function of time), m

\mathbf{x}	position vector (variable distribution), m
\mathbf{y}	position vector at the initial time instant (variable distribution), m
λ	thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$
ρ	density of fluid, kg m^{-3}
ρ_A	partial density (concentration) of component A, kg m^{-3}
τ	time, s

Subscripts

A	related to component A
i	related to i-th particle
j	related to j-th particle
r	related to interparticle distance
T	related to turbulent regime
1	related to a single particle
2	related to a pair of particles

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