Using the Deductive - Inductive Method to Analyze Diffusion Mechanisms in Complex Systems

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Abstract: This article discusses using quasi-chemical formalism to describe nonlinear multicomponent diffusion for analyzing experimental curves of the dependence of diffusion coefficients on component concentrations in complex (e.g., biological) systems. The proposed mathematical model allows us to establish the dependence of the partial coefficients of self-diffusion and inter-diffusion on the components' concentrations in a multicomponent system.

Keywords: diffusion, complex system, stoichiometry of an elementary act, diffusion mechanism, nonlinear diffusion coefficient.

1. Introduction

In our earlier studies, we proposed a general quasi-chemical approach for describing nonlinear multicomponent diffusion in complex systems [1, 2] and showed the suitability of the developed formalism in describing phenomena in complex biological systems that are limited by diffusion [3].

The degree of the system's complexity is determined by the total number of elements diffusing in the system with different geometric and molecular structures, the degree of chemical affinity between these elements, as well as the dynamic properties of the partial chemical potentials coexisting in the studied microelement system. It is important to note that, in particular, binding affinity is the key to assessing the biological processes that underlie intermolecular interactions, structural biology, and the relationship of structures and functions.

This approach, based on the idea of the mechanism of the elementary diffusion act and borrowed from chemical kinetics, was developed to describe nonlinear multicomponent diffusion. It allows us to construct a matrix of diffusion coefficients, the members of which represent all possible variants of crisscrossed coefficients of diffusion. It was shown that diffusion coefficients have the form of a polynomial function of the concentrations of the system components. This approach differs from the generalized diffusion equations for multicomponent systems based on the Fick law, the application of which often leads to discrepancy (balance relations are violated). This formalism allows us to perform the numerical modeling of complex diffusion processes in multicomponent systems.

The physical idea of the quasi-chemical representation of diffusion in solids belongs to Yakov Frenkel [4, 5]. He introduced both the vacancy and the interstitial mechanisms of diffusion and found some rate constants from experimental data. Thirty years later, F.C. Frank and D. Turnbull developed the Frenkel theory further [6]. They studied the very rapid diffusion of copper in germanium. They proposed that the copper could be dissolved into two states, interstitial and substitutional. For the interstitial state the solubility of copper is two orders of magnitude less and the diffusivity many orders of magnitude greater than in the substitutional state. The conversion of these states is effected by lattice vacancies. The quasi-chemical theory of diffusion and viscosity was also developed by H. Eyring with co-authors [7]. Eyring developed the theory of absolute reaction rates for chemical reactions in gases [8] and in condensed phase [9] and then applied these ideas to transport phenomena. In this theory, the transport process is represented by an ensemble of elementary events. Each elementary event is represented by the creation or disintegration of an activated complex. The rate of the elementary process is given by the concentration of activated complexes, multiplied by the rate at which they decompose. The main constructive hypothesis is that it is possible to calculate the concentration of activated complexes by equilibrium statistical thermodynamics: the complex concentration is in quasiequilibrium with the stable components. Each complex has its "internal translational" degree of freedom. On the surface of potential energy, this corresponds to the "reaction path". Complexes move along this path. The velocity of this motion is assumed to be just a thermal velocity and is proportional to \sqrt{T} . The additional reaction path degree of freedom has its own kinetic energy and, therefore, increases the complex heat capacity. We have to consider this in calculating the equilibrium constant. Collective models of diffusion were proposed too. One of the earliest collective models is the Z. Jeffries "ring mechanism" with 4 or more atoms. More details on the history of solid-state diffusion are presented in the review [10] and in a modern textbook [11]. On the surface, there are various mechanisms for collective diffusion [12] as well. Elementary events for these mechanisms involve many atoms simultaneously. A dynamic description of nonlinear multicomponent diffusion requires a unified framework that should satisfy basic physical principles.

2. The Mechanisms of Diffusion Jumps

We represent the physical space as a network of compartments [1]. Each compartment is modeled as a cubic cell with an edge size l. The stoichiometric equations of diffusion describe the interaction of two neighboring cells. To distinguish the quantities related to these two cells we use the upper indexes I and II.

$$A^{\mathrm{I}}, N^{\mathrm{I}}, c^{\mathrm{I}}$$
 $A^{\mathrm{II}}, N^{\mathrm{II}}, c^{\mathrm{II}}$

Figure 1: Cell Jump Model

The mechanism of diffusion is defined as a list of elementary transitions between cells described by their stoichiometric equation. Since diffusion is a sort of jumping reaction on the border, for these jumps the stoichiometric equation is written as:

$$\sum_{i} \alpha_{ri}^{I} A_{i}^{I} + \sum_{i} \alpha_{ri}^{II} A_{i}^{II} \rightarrow \sum_{i} \beta_{ri}^{I} A_{i}^{I} + \sum_{i} \beta_{ri}^{II} A_{i}^{II}, \qquad (1)$$

where *r* is the number of processes, $\alpha_{ri}^{I,II}$ and $\beta_{ri}^{I,II}$ are the stoichiometric coefficients which indicate the number of particles in cells involved in the process. The direction of changes in the elementary event (1) is defined by two stoichiometric vectors

$$\gamma_{ri}^{I} = \beta_{ri}^{I} - \alpha_{ri}^{I}; \quad \gamma_{ri}^{II} = \beta_{ri}^{II} - \alpha_{ri}^{II}.$$
 (2)

Coefficients $\alpha_{ri}^{I,II}$; $\beta_{ri}^{I,II}$ are nonnegative. Usually, we assume that they are integers but, in some situations, real numbers are needed.

Elementary events (1) describe diffusion and do not include the transformation of components (reactions). Therefore, for each *i*, the amount of A_i in the system $(A_i^{I} + A_i^{II})$ should not change. This means exactly that for all *i*, *r*

$$\alpha_{ri}^{I} + \alpha_{ri}^{II} = \beta_{ri}^{I} + \beta_{ri}^{II}.$$
(3)

Within the framework of the Cell Jump Model (Fig.1), the description of an elementary act by means of a stoichiometric equation can be illustrated through the following schemes:



(a) Simple diffusion: a particle from cell I jumps into cell II and inversely





(b) Jumps to free places: a particle from cell I jumps to free place in cell II and inversely



(c) Jumps with clustering: two particles attract the third one

Figure 3: Elementary acts of diffusion, examples.

The composition of each cell is vector $N^{I,II}$. Components of this vector $N^{I,II} = V^{I,II}c^{I,II}$ are the amounts of A_i in the corresponding cell and $V^{I,II}$ are the volumes of the cells. We describe the dynamics of the compositions of two cells by the equations:

$$\frac{dN^{I}}{dt} = -\frac{dN^{II}}{dt} = S^{I,II} \sum_{r} \gamma_{r} w_{r}(c^{I}, c^{II}) \qquad , \qquad (4)$$

where S is the boundary area between two cells and w_r is the process's rate. For many cells, the equations are the same, but with more pairs of cells interacting, more terms are used.

If there are many cells then

A^I, N^I, c^I	A ¹¹ , N ¹¹ , c ¹¹	

Figure 4: Cell Jump Model with first surroundings.

$$\frac{dN^{I}}{dt} = \sum_{J} S^{I,J} \sum_{r} \gamma_{r} w_{r}(c^{I}, c^{J})$$
(5)

with summation through all interacting pairs (I, J).

The rates are intensive variables and should be defined as functions of concentrations or chemical potentials. The crucial question is: how to describe function $w_r(c^{I}, c^{II})$ where $c^{I,II}$ are concentrations components in cells.

The real physics of diffusion may be more complicated. For example, the intensity of jumps and the reaction rate $w_r(c^{I}, c^{II})$ may depend not only on (c^{I}, c^{II}) but also on the surrounding. For example, direct simulation of the jumps on the surface [13] demonstrates that the influence of the surrounding is crucial for structures and critical effects on the surface.

For each process (1) there is the *space-inverted process* that is defined simply by changing I to II and vice versa. We mark the quantities for the space-inverted processes by 0. For example, $\gamma' = -\gamma$. The *detailed space-inversion symmetry* requires that the rate functions for them should differ just by the transposition of the vectors of variables, c^{I} , c^{II} :

$$w'_r(c^{\rm I}, c^{\rm II}) = w_r(c^{\rm I}, c^{\rm II}).$$
 (6)

This requirement of *detailed space symmetry* allows us, in particular, to exclude various types of advection and transport driven by external force. Diffusion, by its definition, is driven by the gradients of the concentrations (or, in the thermodynamic approach, by the gradients of the chemical potentials). This is not the only way to formulate pure diffusion equations without advection. Another possibility is, for example, diffusion systems with complex balance.

3. Mass Action Low (MAL) Equations for Diffusion

Let us consider the system of stoichiometric equations (1) as a reaction mechanism for MAL [1].

If we apply MAL then the rate of the elementary diffusion process is

$$w_r(c^I, c^{II}) = k_r \prod_i (c_i^I)^{\alpha_{ri}^I} \prod_i (c_i^{II})^{\alpha_{ri}^{II}} .$$
(7)

For example, for Fick's diffusion, we have two elementary processes, $A_i^I \rightarrow A_i^{II}$ and $A_i^{II} \rightarrow A_i^{II}$

The corresponding reaction rates are $k_1 c_i^I$ and $k_2 c_i^{II}$. Equations (5) give

$$\frac{dN_i^I}{dt} = -S^{I,II}k_1c_i^I + S^{I,II}k_2c_i^{II} \quad .$$
(8)

The diffusion processes for which *space-inverted elementary processes coincide with the inverse processes* have a fundamental property: The entropy production is positive for the corresponding mass action law diffusion equations.

There are three ways to define the rate functions: from a phenomenological law (like the massaction law), from thermodynamics (like the generalized mass action law) or by direct stochastic simulation of particles jumps in cells (as in the Gillespie approach [14, 15]).

In our research, we focus on the first two approaches. Therefore, we consider our lattice model as a semi-discrete model (discrete in space and continuous in time). For this semi-discrete model, the system of kinetic equations (5) describes diffusion. The continuous limit of these equations gives us the diffusion PDE.

The discrete scheme itself can be serve as a computational model.

A couple of simple examples can clarify our approach:

- Simple diffusion $A_i^{I} \rightarrow A_i^{II}$ and $A_i^{II} \rightarrow A_i^{I}$ with the same rate constants. Particles jump into the neighbor cells. For perfect mixtures, $w_r = kc_i^{I}$, $w'_r = kc_i^{II}$ and in the continuous limit we get Fick's law as the first Taylor approximation. In this approximation, D = kl where *l* is the cell size.
- Jumps to free places $A_i^{I} + Z^{II} \rightarrow A_i^{II} + Z^{I}$ and $A_i^{II} + Z^{I} \rightarrow A_i^{I} + Z^{II}$. According to the mass action law $w_r(c_i^{I}, c_i^{II}) = kc_i^{I}z^{II}$, $w'_r(c_i^{I}, c_i^{II}) = kc_i^{II}z^{II}$, where *z* is the concentration of free places. In the first Taylor approximation $J = -kl(z\nabla c_i c_i\nabla z)$, and we get the model proposed in [16])

To get the continuous limit, we take $c^{I} = c(x)$, $c^{II} = c(x + l)$ and use the Taylor expansion: $c(x + l) = c(x) + l\partial_{x}c + o(l)$. If we consider a sequence of cell representations of diffusion with various l then, for the invariance of the first order, the *scaling rule* should be implemented: D = kl does not change with a size change, therefore, the rate constant k depends on l : k = D/l.

It is not always possible to keep only to the first order. If this approach gives a negative diffusion coefficient then for regularity, we have to keep the higher derivatives. For example, let us take the diffusion mechanism with attraction:

$$A_i^{\rm I} + 2A_i^{\rm II} \to 3A_i^{\rm II} \quad . \tag{9}$$

The space-inverted process in this case does not coincide with the inverse one. If we change the upper indexes (I to II and II to I) then we obtain

$$2A_i^{\rm I} + A_i^{\rm II} \to 3A_i^{\rm I} \quad . \tag{10}$$

This mechanism means that two particles attract the third one. The reaction rates are:

$$w_r = k_r c_i^{\rm I} (c_i^{\rm II})^2$$
, $w_r' = k_r (c_i^{\rm I})^2 c_i^{\rm II}$. (11)

The flux of A_i from the first cell to the second one is

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$$J = w_r - w'_r = k_r c_i^I c_i^{II} (c_i^{II} - c_i^I)$$
 (12)

Therefore, to first order we have

$$J = klc^2 \,\nabla c = \frac{1}{3}kl\nabla c^3,\tag{13}$$

the sign is opposite to standard diffusion. This flux goes in the direction of gradients.

The diffusion equation is

$$\frac{\partial c}{\partial t} = -kldiv(c^2 \nabla c) = kl \frac{1}{3} \Delta c^3 \quad . \tag{14}$$

Of course, if we take the mechanism (n > 1):

$$A_i^{\rm I} + nA_i^{\rm II} \to (n+1)A_i^{\rm I}, \ nA_i^{\rm I} + A_i^{\rm II} \to (n+1)A_i^{\rm I},$$
 (15)

then we get the equation

$$\frac{\partial c}{\partial t} = -kl(n-1)div(c^n \nabla c) = -kl\frac{n-1}{n+1}\Delta c^{n+1} \quad . \tag{16}$$

This diffusion process has two properties: first, it goes along gradients and all deviations from the uniform state will increase. Second, this diffusion is slow for small concentrations (the diffusion coefficient goes to 0 when c approaches 0 and accelerates with the increased concentration.

The equation $\partial_t c = -D\Delta c^n (n > 1)$ admits a family of self-similar solutions with bounded support, which collapse in finite time. These solutions have the form

$$c(\tau) = \frac{A}{\rho^q} \phi\left(\frac{r}{\rho}\right),\tag{17}$$

where

- τ is the time until collapse;
- q is the dimension of space (usually, q = 1, 2 or 3);
- ρ is the radius of the sphere, outside of which the solution is zero

$$\rho = B(D\tau)^{\frac{1}{q(n-1)+2}};$$
(18)

- $\phi(\vartheta) = (1 \vartheta)^{\frac{1}{n-1}}$ for $\vartheta < 1$ and $\phi(\vartheta) = 0$ if $\vartheta \ge 1$;
- The constants A, B depend on q, n and the total amount $N = \int c(x) dx$.

This is the so-called Barenblatt solution [17] for the equation of porous media $\partial_{\tau} c = +D\Delta c^n$. Such solutions were used to analyze an explosion that starts from a singularity for

equations $\partial_t c = +D\Delta c^n$ (the classical review of self-similar solutions was published by Barenblatt and Zeldovich [18]).

The cell model of diffusion with attraction (9) for a finite number of cells of a given size l is a rather regular system of nonlinear ODE, but to the first order of the Taylor expansion in l the PDE (14) produces a singularity in an arbitrarily short time from smooth initial data. The second order Taylor approximation adds nothing because the even terms in l cancel out if we take into account the cell's left and right neighbors. The third order Taylor expansion gives a regularized equation:

$$J = J = w_r - w'_r = klc^2 \frac{\partial}{\partial x} \left(c + \frac{l^2}{3} \frac{\partial^2 c}{\partial x^2} \right) + o(l^3)$$
$$\frac{dc}{dt} = -kl \frac{\partial}{\partial x} c^2 \frac{\partial}{\partial x} \left(c + \frac{l^2}{3} \frac{\partial^2 c}{\partial x^2} \right) .$$
(19)

This is an example of the Cahn–Hilliard type equation for spinodal decomposition with the regularizing term $-div(c^2 grad \Delta c)$. In this equation, the cell size cannot be eliminated by scaling. The length *l* is the "regularization length". All inhomogeneities of size smaller than *l* are smoothed by the biharmonic term.

As we can see, the mass action law and the cell representation of the elementary acts of diffusion give the opportunity to model the Cahn–Hilliard type phase separation. Nevertheless, the approach based on the non-perfect thermodynamic potential gives a better representation of the basic physics and does not require complicated elementary processes. Just the simplest Fick scheme,

$$A_i^{\rm I} \to A_i^{\rm II}, \quad A_i^{\rm II} \to A_i^{\rm I} \tag{20}$$

with the non-perfect Ginzburg–Landau free energy gives the Cahn–Hilliard equation. The diffusion mechanism with attraction (9) differs from the elementary Fick mechanism and from the mechanism of jumps to free places. The dynamic difference is obvious, the diffusion mechanism with attraction generates instabilities of the homogeneous state, clustering and singularities. On the other hand, Fick's law and the mechanism of jumps to free places allow a global Lyapunov functional and, in the systems without external fluxes, lead to homogeneous equilibrium.

These mechanisms also have a very important structural difference. If we look at the direct and the space-inverted processes then we find that for the first two mechanisms, the space inverted processes coincide with the inverse processes, which we get just by inverting the arrow (or by the exchange α and β coefficients in the stoichiometric equations (1)). For the elementary processes with attractions, the inverse processes are processes with repulsion:

$$3A_i^{\mathrm{II}} \to A_i^{\mathrm{I}} + 2A_i^{\mathrm{II}}, \qquad 3A_i^{\mathrm{I}} \to 2A_i^{\mathrm{I}} + A_i^{\mathrm{II}} \quad . \tag{21}$$

The diffusion processes for which *space-inverted elementary processes coincide with the inverse processes* have a fundamental property: The entropy production is positive for the corresponding mass action law diffusion equations.

4. Continuous Diffusion Equation

Let us consider an elementary process together with its space-inverted process

$$\sum_{i} \alpha_{ri}^{\mathrm{I}} A_{i}^{\mathrm{I}} + \sum_{i} \alpha_{ri}^{\mathrm{II}} A_{i}^{\mathrm{II}} \rightarrow \sum_{i} \beta_{ri}^{\mathrm{I}} A_{i}^{\mathrm{I}} + \sum_{i} \beta_{ri}^{\mathrm{II}} A_{i}^{\mathrm{II}}$$
$$\sum_{i} \alpha_{ri}^{\mathrm{I}} A_{i}^{\mathrm{II}} + \sum_{i} \alpha_{ri}^{\mathrm{II}} A_{i}^{\mathrm{I}} \rightarrow \sum_{i} \beta_{ri}^{\mathrm{I}} A_{i}^{\mathrm{II}} + \sum_{i} \beta_{ri}^{\mathrm{II}} A_{i}^{\mathrm{II}}$$
(22)

The reaction rates are

$$w_{r}(c^{\mathrm{I}}, c^{\mathrm{II}}) = k_{r} \prod_{i} \left[\left(c_{i}^{\mathrm{I}} \right)^{\alpha_{ri}^{1}} \prod_{i} \left[\left(c_{i}^{\mathrm{II}} \right)^{\alpha_{ri}^{\mathrm{II}}} \right] \right]_{i}$$
$$w_{r}(c^{\mathrm{I}}, c^{\mathrm{II}}) = w_{r}(c^{\mathrm{II}}, c^{\mathrm{I}}) = k_{r} \prod_{i} \left(c_{i}^{\mathrm{II}} \right)^{\alpha_{ri}^{\mathrm{II}}} \prod_{i} \left(c_{i}^{\mathrm{II}} \right)^{\alpha_{ri}^{\mathrm{II}}}$$
(23)

where we take $k'_r = k_r$ due to the symmetry in space.

To first order in l, the flux vector for A_i in this process is

$$J_{ri} = -\gamma_{ri} \Big[w_r(c(x), c(x+l)) - w_r(c(x+l), c(x)) \Big]$$

$$= -l\gamma_{ri} \sum_j \left(\frac{\partial w_r(c^{\mathrm{I}}, c^{\mathrm{II}})}{\partial c_j^{\mathrm{II}}} \Big|_{c^{\mathrm{I}} = c^{\mathrm{II}} = c(x)} - \frac{\partial w_r(c^{\mathrm{I}}, c^{\mathrm{II}})}{\partial c_j^{\mathrm{I}}} \Big|_{c^{\mathrm{I}} = c^{\mathrm{II}} = c(x)} \right) \nabla c_j(x)$$

$$= l\gamma_{ri} w_r(c(x), c(x)) \sum_j \frac{\alpha_{rj}^{\mathrm{II}} - \alpha_{rj}^{\mathrm{I}}}{c_j} \nabla c_j(x)$$

$$= -lk\gamma_{ri} \left(\prod_q c_q^{\alpha_{rq}^{\mathrm{I}} + \alpha_{rq}^{\mathrm{II}}} \right) \sum_j \frac{\alpha_{rj}^{\mathrm{II}} - \alpha_{rj}^{\mathrm{I}}}{c_j} \nabla c_j(x).$$
(24)

Here, $\gamma_{ri} = \beta_{ri}^{I} - \alpha_{ri}^{I}$ (input minus output in the first cell); the minus in front of the formula appears because the direction of flux from cell I to cell II (from x to (x + l)) is positive.

The factor $1/c_j$ never leads to a singularity in the flux because c_j enters in the monomial $\prod_q c_q^{\alpha_{rq}^I + \alpha_{rq}^{II}}$ with the power $\alpha_{rj}^{I} + \alpha_{rj}^{II}$. This power is strictly positive if the coefficient $(\alpha_{rj}^{II} - \alpha_{rj}^{I})$ is not zero.

The proper scaling of k for grid refinement or coarsening is kl = d = const in order not to change the first order expression for flux (24).

According to (24), the matrix of diffusion coefficients for the elementary process (22) (together with its space-inverted process) is

$$D_{rij}(c) = d\left(\prod_{q} c_q^{\alpha_{rq}^{\mathrm{I}} + \alpha_{rq}^{\mathrm{II}}}\right) \frac{\gamma_{ri} \left(\alpha_{rj}^{\mathrm{II}} - \alpha_{rj}^{\mathrm{I}}\right)}{c_j},\tag{25}$$

where d = const (= kl).

The corresponding diffusion equations have the divergent form:

$$\frac{\partial c}{\partial t} = div(D(c)\nabla c), \tag{26}$$

where c is the vector of concentrations and D is the matrix of diffusion coefficients (25).

It might be useful to represent the flux (24) similarly to the Teorell formula [19, 20]. For this purpose, let us collect under ∇ the terms that represent the chemical potential in perfect media: $\mu = RT lnc + \mu_0$.

We assume that T and μ_0 are constant in space. With these conditions,

$$J_{ri} = -\frac{lk}{RT} \gamma_{ri} \left(\prod_{q} c_{q}^{\alpha_{rq}^{\mathrm{I}} + \alpha_{rq}^{\mathrm{II}}} \right) \sum_{j} (\alpha_{rj}^{\mathrm{II}} - \alpha_{rj}^{\mathrm{I}}) \nabla \mu_{j} (x) .$$
 (27)

The deductive method described above for analyzing the mechanisms of the complex process of multicomponent diffusion does not allow us to answer the important question of determining the stoichiometric coefficients of the dominant (basic) mechanism that determines the course of diffusion transfer.

However, knowing the numerical values of these coefficients is very important from both a theoretical and a practical point of view. Firstly, it can be seen from expression (25) for the matrix of diffusion coefficients that these quantities determine what sign each member of the matrix has. Secondly, these values determine the degree of dependence of the diffusion coefficient on the concentrations of the components of a complex system. To solve this problem adequately, the experimental and theoretical methods for establishing the concentration dependence of the diffusion coefficients should be combined.

Such an approach can be called the inductive-deductive method of analyzing the mechanisms of diffusion transfer.

5. Inductive-deductive method of analyzing the mechanisms of the diffusion process

We proceed to constructing a mathematical scheme to describe nonlinear multicomponent diffusion by analyzing the experimental curves of the dependence of the diffusion coefficients on the diffusant's concentration in complex (for example, biological) systems. The concentration curves recorded under specific conditions reveal the degree of dependence of the intensity of diffusion transfer on the components of the concentration vector of a multicomponent system. Therefore, deciphering these curves will allow us to establish the degree of dependence (the law of dependence) of each diffusion coefficient on the concentration of particles participating in each elementary event of the diffusion jump.

For simplicity, we restrict ourselves to approximating the pairwise interaction of diffusing microparticles and assume the absence of chemical transformations.

In approximating the pair wise interaction of flows of various components, the stoichiometric equation that describes an elementary diffusion event within the framework of the cell-hopping model (see Fig. 1) will have the following form:

$$n_i A_i^{\mathrm{I}} + n_j A_j^{\mathrm{II}} \to n_i A_i^{\mathrm{II}} + n_j A_j^{\mathrm{I}} \quad . \tag{28}$$

Under the assumption that the microdescription is invariant to time reversal, each process (28) also has an inverse process associated with it:

$$n_i A_i^{\mathrm{II}} + n_j A_j^{\mathrm{I}} \to n_i A_i^{\mathrm{I}} + n_j A_j^{\mathrm{II}} .$$
⁽²⁹⁾

The expression for the density vector of the total flux of the i- th substance, diffusing according to the mechanism (28) and (29), will have the following form:

$$\vec{J}_{i} = k_{1} n_{i} n_{j} c_{i}^{n_{i}} c_{j}^{n_{j}-1} \vec{\nabla} c_{j} - k_{2} n_{i}^{2} c_{i}^{n_{i}-1} c_{j}^{n_{j}} \vec{\nabla} c_{i} , \qquad (30)$$

where k_1 and k_2 are the rate constants of elementary diffusion events by the mechanism (28) and (29); c_i , c_j are the concentrations of the components involved in the elementary act of diffusion.

By analogy with Fick's law, from (30) we obtain, respectively, the expression for the coefficient of "self-diffusion" (coefficient before $\vec{\nabla}c_i$):

$$D_{ii}(c_i, c_j,) = k_2 n_i^2 c_i^{n_i - 1} c_j^{n_j}$$
(31)

and for the coefficient of "mutual diffusion" (coefficient before $\vec{\nabla} c_j$):

$$D_{ij}(c_i, c_j,) = k_1 n_i n_j c_i^{n_i} c_j^{n_j - 1}.$$
(32)

Thus, if experimental curves $D_{ii} = D_{ii}(c_i, c_j)$ or $D_{ij} = D_{ij}(c_i, c_j)$ are obtained, then from the form of these curves and using (31) or (32) we can determine the most probable values of stoichiometric coefficients n_i and n_j . Summing up our results, we conclude that the general quasi-chemical approach for describing nonlinear multicomponent diffusion allows us to develop a mathematical model for processing the data of a diffusion experiment and obtaining information on the stoichiometry of the dominant diffusion mechanisms that determine the course of the process in each case.

6. Conclusion

Processing the results of diffusion experiments is a complex and finally unsolved problem. First, the laws of diffusion are described by the sums of the series – which are bulky and poorly converging. Moreover, in many real-life situations, the initial differential equations cannot be expressed in elementary functions (for example, sequential diffusion in a layered medium) or, in principle, have no solution (for example, diffusion + a second-order chemical reaction).

Currently, many branches of science and technology require the optimal control of unsteady mass transfer in chemically - or adsorption-active heterogeneous media with varying composition and structure in space and time. Such control is inconceivable without knowledge of the mechanism of the transfer of low molecular weight substances in a complex system, without selecting an adequate diffusion model and without calculating its parameters and their errors.

We have demonstrated how an approach based on the mechanism of the elementary diffusion act allows diffusion to be described in a multicomponent system. The formalism developed in this work allows the effective numerical modelling of complex diffusion processes in multicomponent systems.

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