B – Mathematical model of interdiffusion

In this section formulation of the model, i.e., the initial boundary-value problem for the interdiffusion in multi-component non-ideal open systems is presented in a classical way, i.e., presenting data, physical laws, initial and boundary conditions and finally the unknowns to be calculated.

Data

1. $d > 0$ - a thickness of the system (see Figure 1);
2. $c_1^o = c_1^o(x), \ldots, c_r^o = c_r^o(x)$ - the initial distributions of the components $c_i^o : [-\Lambda, \Lambda] \to \mathbb{R}_+,\ i = 1, \ldots, r$, such that:

$$c = \sum_{i=1}^{r} c_i^o = const.$$

where r-number of the components in the system and $c > 0$ is the molar concentration of the system;

3. $D_1^* = D_1^*(c_1, \ldots, c_r), \ldots, D_r^* = D_r^*(c_1, \ldots, c_r)$ - self diffusion coefficients of the components, which may depend on components’ densities
4. $a_1 = a_1(c_1, \ldots, c_r), \ldots, a_r = a_r(c_1, \ldots, c_r)$ - the activities of the components as functions of components’ concentrations;
5. $\hat{t}$ - the time of the process duration;
6. $j_{iL}, j_{iR}[0, \hat{t}] \to \mathbb{R}\ \ i = 1, \ldots, r$ - evolution of mass flow of the i-th component through the left and right boundary. As a consequence of constant concentration of the system these fluxes satisfy the following relation:

$$\sum_{i=1}^{r} j_{iL}(t) = \sum_{i=1}^{r} j_{iR}(t) \quad for \ \ t \in [0, \hat{t}].$$

Therefore only $2r - 1$ fluxes are independent.

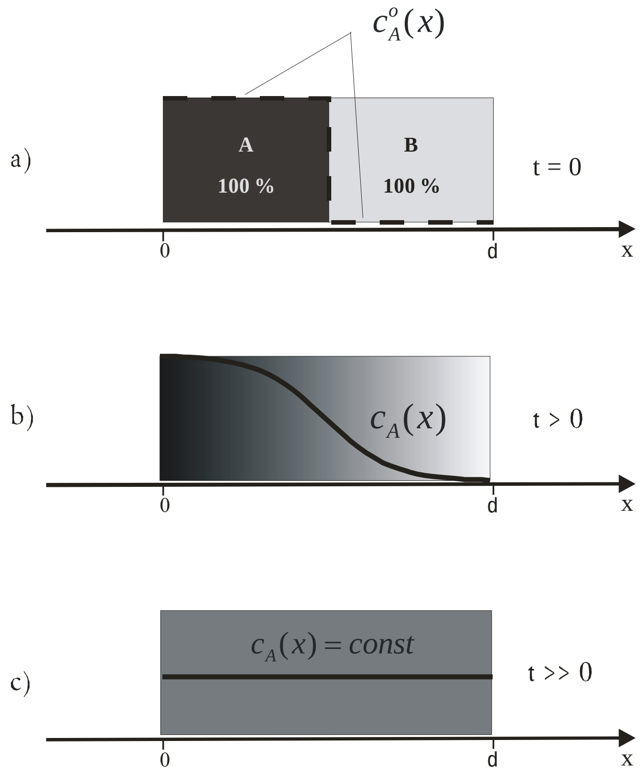

Figure 1 Schematic graph of interdiffusion in a binary diffusion couple A/B: (a) initial state – initial density profile of the component *A*, $c_A^o(x)$ at $t = 0$, (b) density profile $c_A(x)$ after some time $t > 0$ and (c) for long time $t \gg 0$

Physical Laws

1. Law of the mass conservation of an i-th element. That law tells that a local change of molar concentration of an i-th element is a result of its net in- or outflow only:

$$\frac{\partial c_i}{\partial t} + \frac{\partial J_i}{\partial x} = 0 \quad i = 1, \ldots, r. \tag{1}$$

Following Darken's drift flow idea [1], it is postulated that the flux of an i-th element, J_i, is a sum of its diffusion flux, J_i^d, and the drift flux, $(c_i \upsilon)$:

$$J_i := J_i^d + c_i \upsilon. \tag{2}$$

In the next sections it will be shown that the effective solution of Darken's model for multi-

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[1] L.S. Darken, Trans. AIME, 180, 430 (1948)

component systems can be obtained when the diffusion flux is expressed by [2]:

$$J_i^d = B_i c_i \sum_j F_j, \tag{3}$$

where B_i is the mobility of an i-th element and $\sum_j F_j$ - the sum of the internal or external forces which act on a system.

2. A postulate of the constant molar volume of the system. Consequently the molar concentration of the system being a sum of the concentrations of all elements at any position for every time is constant:

$$c_1 + \ldots + c_r = c = const. \tag{4}$$

Initial and boundary conditions

1. The initial concentration distributions of the components in the system:

$$c_i^o(x) = c_i(0,x) \qquad for\ x \in [-\Lambda, \Lambda],\ i = 1,\ldots,r.$$

2. The following boundary conditions are postulated:

$$\begin{gathered} J_i\left(t,-\Lambda\right) = j_{iL}(t), \qquad J_i\left(t,+\Lambda\right) = j_{iR}(t), \\ for\ t \in [0,\hat{t}\,],\ i = 1,\ldots,r. \end{gathered} \tag{5}$$

In the open system the functions, $j_{iL}(t)$ and $j_{iR}(t)$, have to be known. They can be calculated e.g., from the known rate of reactions at the boundary or from the experimental data. In the closed system the gradients of all the components at both boundaries vanish, i.e., the flux of an i-th component at the boundary equals zero:

$$J_i\left(t,\pm\Lambda\right) = 0 \qquad for\ t \in [0,\hat{t}\,],\ i = 1,\ldots,r.$$

The unknowns

1. Molar concentrations of the components as functions of time and position, $c_i(t, x),\ i = 1,\ldots,r$.
2. A drift velocity as a function of time and position, $\upsilon(t,x)$.

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[2]M. Planck, Ann. Phys. Chem. (Wiedemann) 39, 161 (1890)

The Diffusion Flux Formula

In this section the Eq. (3) describing the diffusion flux will be rearranged into the form, which allows obtaining an effective numerical solution. It is generally accepted, that the diffusion force in the Eq. (3) can be described as the spatial gradient of the chemical potential, μ_i, and the corresponding flux can be expressed by the following expression

$$J_i^d = -B_i c_i \frac{\partial \mu_i}{\partial x}. \tag{6}$$

The thermodynamic definition of the chemical potential is

$$\mu_i(c_1,\ldots,c_r) = \mu_i^o + RT \ln a_i(c_1,\ldots,c_r), \tag{7}$$

where k – the Boltzmann's constant, T – an absolute temperature and μ_i^o is the standard-state chemical potential usually referred to unit thermodynamic activity $(a_i = 1)$. The gradient of the chemical potential can be calculated as follows

$$\frac{\partial \mu_i}{\partial x}(c_1,\ldots,c_r) = \sum_{j=1}^{r} \frac{\partial \mu_i}{\partial c_j}(c_1,\ldots,c_r)\frac{\partial c_j}{\partial x}. \tag{8}$$

Using Eqs. (6),(7) and (8) the diffusion flux can be expressed in the form

$$J_i^d = -B_i RTc_i \sum_{j=1}^{r} \frac{\partial \ln a_i}{\partial c_j}\frac{\partial c_j}{\partial x}. \tag{9}$$

Substituting the Nernst-Einstein relation $\left(D_i^* = B_i kT\right)$ into Eq. (9), we get

$$J_i^d = -D_i^* c_i \sum_{j=1}^{r} \frac{\partial \ln a_i}{\partial c_j}\frac{\partial c_j}{\partial x}. \tag{10}$$

Above diffusion flux formula can be rearranged to the final form

$$J_i^d = -\sum_{j=1}^{r} D_{ij}\frac{\partial c_j}{\partial x}, \tag{11}$$

where the partial intrinsic diffusivities, D_{ij}, are defined as follows

$$D_{ij}(\varrho) := D_i^*(c_1,\ldots,c_r)\, c_i \frac{\partial \ln a_i}{\partial c_j}(c_1,\ldots,c_r). \tag{12}$$

One can notice that in the ideal system, when activity coefficients equal one, the diffusion flux becomes

$$J_i^d = -D_i^* \frac{\partial c_i}{\partial x} \,. \tag{13}$$