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**ENTROPY PRODUCTION
 IN THE DIFFUSION OF A MARGULES
 SOLUTION IN A PLANE-PARALLEL PORE**

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An expression for the entropy production in the case of the facilitated diffusion of a Margules binary solution has been obtained. A stabilizing effect with respect to the solution concentration gradient was revealed. The entropy contributions to changes of the thermodynamic potentials at the mixing are found to play a dominant role in the transformation of the character of entropy production in the system.

Keywords: Margules, entropy production.

One of the main tasks of the thermodynamics of irreversible processes as a field theory consists in obtaining the concentration dependence for the entropy production intensity in various irreversible processes in the system [1]. The systems concerned include confined systems such as biological membranes, in which chemical reactions and diffusion processes may take place, meso- and nano-objects, *etc.* This work aims at deriving the expressions for the entropy production in the case of a non-ideal solution, namely, when the solution is described by the Margules empirical model [2].

Note that models of non-ideal solutions may contain constants that are not always determined in terms of the intermolecular potentials in solutions. In the case of binary non-electrolyte solutions with a non-valence interaction between molecules, the relation between the coefficients in the Margules model and the corresponding intermolecular potential was obtained with the help of perturbation theory [3]. In works [4, 5], a general expression for the diffusion equation was obtained, the concentration dependence of the diffusion coefficient was calculated, and the research of the entropy production in confined systems

in the presence of diffusion processes was carried out in the framework of the linear thermodynamics of irreversible processes. In addition, the general equation for the entropy production rate in the presence of diffusion processes was considered, and the model describing the entropy production in a plane-parallel layer with osmotic boundary conditions was developed.

The general equation describing the diffusion in a system with chemical reactions looks like [4]

$$\begin{aligned} \rho \frac{\partial c_k}{\partial t} = & \operatorname{div} \left(\sum_{i=1}^n \sum_{\substack{j=1 \\ j \neq k}}^n L_{ki} \left[v_i \frac{\partial p}{\partial c_j} + kT \left(\frac{\delta_{ij}}{c_i} + \right. \right. \right. \\ & \left. \left. \left. + \frac{1}{\gamma_i} \frac{\partial \gamma_i}{\partial c_j} \right) \right] \nabla c_j \right) + \operatorname{div} (D_k \nabla c_k) - \rho \mathbf{v} \cdot \nabla c_k + \\ & + \operatorname{div} \left(\sum_{i=1}^n L_{ki} v_i \frac{K_T}{\rho} \nabla \rho + D_T \nabla T \right) + \sum_{i=1}^r M_k \nu_{ki} J_i, \end{aligned} \quad (1)$$

where ρ is the total mass density of the system, t the time, M_k the molar mass of the k -th component, L_{ki} the corresponding kinetic coefficients, p the pressure, δ_{ij} the Kronecker symbol, γ_i the activity of the i -th

component, v_k the partial molar volume, D_k the diffusion coefficient of the k -th component, D_T the Soret coefficient, K_T the isothermal compression modulus, J_i the local rate of the i -th chemical reaction, \mathbf{v} the velocity of the center of mass, ν_k the stoichiometric coefficient, r the number of different chemical reactions, and c_k the concentration of the corresponding component. This equation is the most general form for the equation of diffusion in the presence of chemical reactions and in the absence of external fields and allows the substance flow to be calculated in the general case. If it is applied to a specific model, it is necessary firstly to estimate the influence of various thermodynamic forces on the processes in the system and, afterward, to simplify this equation by excluding terms, which can be neglected.

In work [5], the diffusion flows were described by the expressions

$$\mathbf{J}_k = -D_k \nabla c_k - \sum_{i=1}^n \sum_{\substack{j=1 \\ j \neq k}}^n L_{ki} \left[v_i \frac{\partial p}{\partial c_j} + kT \left(\frac{\delta_{ij}}{c_i} + \frac{1}{\gamma_i} \frac{\partial \gamma_i}{\partial c_j} \right) \right] \nabla c_j - \sum_{i=1}^n L_{ki} v_i \frac{K_T}{\rho} \nabla \rho - D_T \nabla T, \quad (2)$$

and the entropy production in the case of the stationary diffusion in a binary solution is

$$\sigma = L_1 (2k)^2 \left(\frac{dx_1}{dz} \right)^2 \left\{ \left[\frac{1}{x_1} + \frac{\partial}{\partial x_1} \ln \gamma_1 \right] - \frac{v_{10} + kT \frac{\partial}{\partial p} \ln \gamma_1}{v_{20} + kT \frac{\partial}{\partial p} \ln \gamma_2} \left[\frac{\partial}{\partial x_1} \ln \gamma_2 - \frac{1}{1-x_1} \right] \right\}^2. \quad (3)$$

In the case of the diffusion of a binary solution, the plane-parallel membrane of the thickness l contains a substratum (the corresponding thermodynamic variables are designated by subscript 1), which diffuses through the membrane, and a carrier (subscript 2), which cannot go beyond the membrane boundaries. The last circumstance becomes responsible for the so-called facilitated diffusion [6], in which the substratum combines with the "carrier" to form a complex "substratum-carrier", which transfers the substratum through the membrane. Let a temperature gradient in the system be absent. With regard for Eq. (2), the system of equations for the flow J_1 can be presented

in the form [4]

$$\begin{cases} J_1 = -2kL_1 \frac{dx_1}{dz} \left\{ \left[\frac{1}{x_1} + \frac{\partial}{\partial x_1} \ln \gamma_1 \right] + \frac{v_{10} + kT \frac{\partial}{\partial p} \ln \gamma_1}{v_{20} + kT \frac{\partial}{\partial p} \ln \gamma_2} \left[\frac{1}{1-x_1} - \frac{\partial}{\partial x_1} \ln \gamma_2 \right] \right\}, \\ \frac{dx_2}{dz} = -\frac{dx_1}{dz}, \\ \frac{dp}{dz} = -\frac{2kT \left[\frac{\partial}{\partial x_1} \ln \gamma_2 - \frac{1}{1-x_1} \right] dx_1}{v_{20} + kT \frac{\partial}{\partial p} \ln \gamma_2} \frac{dx_1}{dz}, \end{cases} \quad (4)$$

where k is the Boltzmann constant, v_{10} and v_{20} are the volumes of the corresponding pure substances in the solution per particle, and L_1 is the diagonal kinetic coefficient in the matrix of phenomenological coefficients L_{ki} (in other words, we consider a case where the cross vector effects such as the thermal diffusion are not taken into account, because, in liquid systems, they are smaller by several orders of magnitude than the direct effects). The analysis of expression (4) shows that, in order to calculate the substance flow and the entropy production in a binary solution in a plane-parallel pore, we must specify the explicit form for the activity coefficient $\gamma_i(T, p, x_1)$. The latter can be calculated with the help of perturbation theory applied to an isobaric-isothermal ensemble [7], which enables the thermodynamic properties of this solution and the character of possible chemical reactions to be described.

In the framework of proposed approach, let us consider the entropy production in the Margules empirical solution model. In this case, the activity coefficients γ_1 and γ_2 can be written down [8] as follows:

$$\begin{aligned} \ln \gamma_1(T, p, x_1) &= \frac{a_1(T, p)}{2} (1-x_1)^2 + \frac{a_2(T, p)}{3} (1-x_1)^3, \\ \ln \gamma_2(T, p, x_1) &= \frac{a_1(T, p) + a_2(T, p)}{2} x_1^2 - \frac{a_2(T, p)}{3} x_1^3, \end{aligned} \quad (5)$$

where $a_1(T, p)$ and $a_2(T, p)$ are dimensionless quantities depending only on the temperature and the pressure of the solution and characterizing the interaction between particles of different components. The proposed Margules equations (5) allow one to describe both symmetric and asymmetric models of a solution. In the framework of the model concerned, the

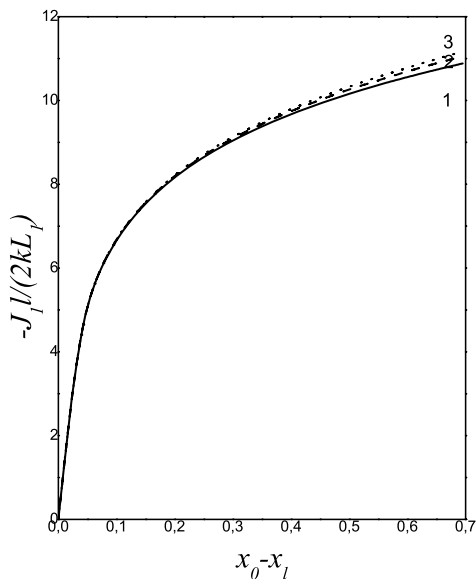


Fig. 1. Dependences of the normalized flow $-\frac{l}{2kL_1}J_1$ on the difference $x_0 - x_l$ for various ratios $\frac{v_{10}}{v_{20}}$ for the Margules solution: $\frac{v_{10}}{v_{20}} = 0.01$ (1), 0.02 (2), and 0.5 (3). The values of other parameters are $a_1 = 3$, $a_2 = 6$, $T = 300$ K, and $v_{10} = 3.8 \times 10^{-29}$ m³. At the right membrane boundary, $x_l = 5 \times 10^{-1}$

behavior of both non-electrolyte solutions and various organic compounds can be described [2]. In this case, the system of equations (4) reads

$$\left\{ \begin{aligned} & J_1 = -2kL_1 \frac{dx_1}{dz} \left\{ \left[\frac{1}{x_1} - a_1(1-x_1) - a_2(1-x_1)^2 \right] + \right. \\ & \left. + \frac{v_{10} + kT \frac{(1-x_1)^2}{2} \frac{\partial a_1}{\partial p} + kT \frac{(1-x_1)^3}{3} \frac{\partial a_2}{\partial p}}{v_{20} + kT \frac{x_1^2}{2} \left(\frac{\partial a_1}{\partial p} + \frac{\partial a_2}{\partial p} \right) - kT \frac{x_1^3}{3} \frac{\partial a_2}{\partial p}} \times \right. \\ & \left. \times \left[\frac{1}{1-x_1} - (a_1 + a_2)x_1 + a_2x_1^2 \right] \right\}, \quad (6) \\ & \frac{dx_2}{dz} = -\frac{dx_1}{dz}, \\ & \frac{dp}{dz} = -2kT \frac{(a_1 + a_2)x_1 - a_2x_1^2 - \frac{1}{1-x_1}}{v_{20} + kT \frac{x_1^2}{2} \left(\frac{\partial a_1}{\partial p} + \frac{\partial a_2}{\partial p} \right) - kT \frac{x_1^3}{3} \frac{\partial a_2}{\partial p}} \frac{dx_1}{dz}, \end{aligned} \right.$$

which is supplemented by the corresponding boundary conditions

$$\begin{cases} x_1(z = 0) = x_0, \\ x_1(x = l) = x_l. \end{cases} \quad (7)$$

After integrating the first equation in system (6) with the boundary conditions (7), we obtain the following expression for the stationary flow J_1 :

$$\begin{aligned} -\frac{l}{2kL_1} J_1 = & \frac{a_1}{2} \{ (1-x_l)^2 - (1-x_0)^2 \} + \frac{a_2}{3} \{ (1-x_l)^3 - \\ & - (1-x_0)^3 \} + \frac{a_2}{3} \{ x_l^3 - x_0^3 \} - \frac{2a_1 + 5a_2}{4} \{ x_l^2 - x_0^2 \} + \\ & + \frac{3}{4} a_2 \left(3 + \frac{\partial a_1}{\partial p} \left(\frac{\partial a_2}{\partial p} \right)^{-1} \right) 3a_1 \{ x_l - x_0 \} + \ln \frac{x_l}{x_0} + \\ & + A \ln \frac{1-x_l}{1-x_0} - B \ln \frac{X-x_l}{X-x_0} - \\ & - C \ln \frac{\frac{2v_{02}}{kTX \frac{\partial a_2}{\partial p}} + \left(X - \frac{3}{2} \left(\frac{\partial a_1}{\partial p} \left(\frac{\partial a_2}{\partial p} \right)^{-1} + v_1 \right) \right) x_l + x_l^2}{\frac{2v_{02}}{kTX \frac{\partial a_2}{\partial p}} + \left(X - \frac{3}{2} \left(\frac{\partial a_1}{\partial p} \left(\frac{\partial a_2}{\partial p} \right)^{-1} + 1 \right) \right) x_0 + x_0^2} - \\ & - D \operatorname{arctg} \frac{X - \frac{3}{2} \left(\frac{\partial a_1}{\partial p} \left(\frac{\partial a_2}{\partial p} \right)^{-1} + 1 \right) + 2x_l}{X_3}, \quad (8) \end{aligned}$$

where

$$\begin{aligned} X = & \frac{1}{2} \left(\frac{\partial a_1}{\partial p} \left(\frac{\partial a_2}{\partial p} \right)^{-1} + 1 \right) + \\ & + \left\{ \frac{3}{2} \frac{v_{20}}{kT} \left(\frac{\partial a_2}{\partial p} \right)^{-1} + \frac{\left(\frac{\partial a_1}{\partial p} \left(\frac{\partial a_2}{\partial p} \right)^{-1} + 1 \right)^3}{8} \right. \\ & + \left. \left\{ \frac{3}{8} \frac{v_{20}}{kT} \left(\frac{\partial a_2}{\partial p} \right)^{-1} \left(\frac{\partial a_1}{\partial p} \left(\frac{\partial a_2}{\partial p} \right)^{-1} + 1 \right)^2 + \right. \right. \\ & \left. \left. + \frac{9}{4} \left(\frac{v_{20}}{kT} \right)^2 \left(\frac{\partial a_2}{\partial p} \right)^{-2} \right\}^{1/2} \right\}^{1/3}, \quad (9) \end{aligned}$$

and the quantities A , B , C , and D are expressed in terms of the parameters of a solution and a pure substance a_1 , a_2 , $\frac{\partial a_1}{\partial p}$, $\frac{\partial a_2}{\partial p}$, v_{10} , and v_{20} . Expressions (3) and (7) make it possible to determine the entropy production in the case of the Margules solution.

In Fig. 1, the dependences of the normalized substance flow diffusing through a membrane on the difference of concentrations at the boundaries of the system, $x_0 - x_l$, are shown for various ratios between the partial volumes of components of the solution at fixed a_1 - and a_2 -values. Figure 2 demonstrates the dependences of the normalized diffusion flow on the difference $x_0 - x_l$ for various values of

parameters a_1 and a_2 . The analysis of the presented results testifies that, at small values of the difference $x_0 - x_l$, the dependence is almost linear. However, if the difference $x_0 - x_l$ grows further, the dependence $J_1(x_0 - x_l)$ deviates substantially from the linear one, and we obtain a stabilizing effect, i.e. the flow starts to depend weakly on the difference of concentrations at the boundaries of the system. The exhibited data testify that, as the ratio between the partial molar volumes of the substance diffusing through the membrane and the solvent diminishes, the stabilizing effect becomes stronger for a larger difference of concentrations at the membrane boundaries.

In Fig. 3, the dependences of entropy production on the difference of concentrations at the boundaries of the system, $x_0 - x_l$, are shown for various ratios between the partial volumes of components in the solution and for two different x_l -values at fixed a_1 - and a_2 -values. The analysis of the presented results shows that, at small values of quantity $x_0 - x_l$, the entropy production practically obeys the square-law dependence. However, at larger values of $x_0 - x_l$, the dependence $\sigma(x_0 - x_l)$ substantially deviates from the quadratic one, and the stabilizing effect takes place, i.e. the entropy production weakly depends on the difference of concentrations at the boundaries. The same effect is also observed if only the entropic terms are taken into account, i.e. for an ideal solution [5]. As should be expected from the analysis of the results obtained for flows, as the ratio between the partial molar volumes of the substance diffusing through the membrane and the solvent diminishes, an insignificant enhancement of the stabilizing effect is observed, when the difference of concentrations at the membrane boundaries increases.

The account of energy contributions to the thermodynamic potentials at mixing in the framework of the Margules solution model allows reverse chemical reactions to be taken into consideration, the latter being a characteristic feature of diffusion processes in biological systems. The presented results point to a considerable difference of the entropy production dependence on the quantity $x_0 - x_l$ from that in a system with a constant diffusion coefficient, for which this dependence is quadratic. Moreover, the analysis of the data obtained testifies that the account of energy contributions to the thermodynamic potentials at mixing results in that the substance flow (Fig. 1)

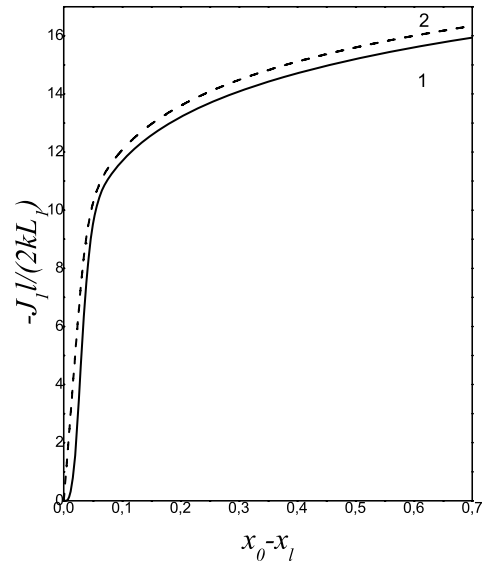


Fig. 2. Dependences of the normalized flow $-\frac{l}{2kL_1}J_1$ on the difference $x_0 - x_l$ for various a_1 - and a_2 -values for the Margules solution: (1) $a_1 = 3, a_2 = 6$ and (2) $a_1 = 5, a_2 = 9$. The values of other parameters are $T = 300$ K, $\frac{v_{10}}{v_{20}} = 0.01$, and $v_{10} = 3.8 \times 10^{-29}$ m³ (1), 0.02 (2), and 0.5 (3). The parameter values are $a_1 = 3, a_2 = 6, T = 300$ K, and $v_{10} = 3.8 \times 10^{-29}$ m³. At the right membrane boundary, $x_l = 5 \times 10^{-3}$

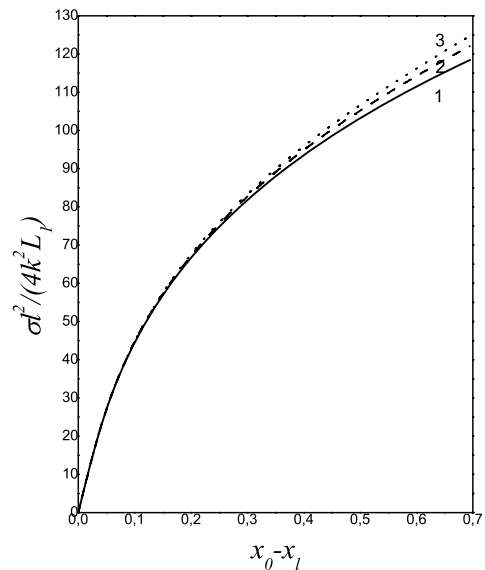


Fig. 3. Dependences of the normalized entropy production $\frac{l^2}{(2k)^2L_1}\sigma$ on the difference $x_0 - x_l$ for various ratios $\frac{v_{10}}{v_{20}}$ for the Margules solution: $\frac{v_{10}}{v_{20}} = 0.01$ (1), 0.02 (2), and 0.5 (3). The values of other parameter are $a_1 = 3, a_2 = 6, T = 300$ K, and $v_{10} = 3.8 \times 10^{-29}$ m³. At the right membrane boundary, $x_l = 5 \times 10^{-5}$

and the entropy production (Fig. 3) start to depend much more weakly on the ratio between the partial volumes of pure substances, $\frac{v_{10}}{v_{20}}$, than in the case of ideal solution [5]. This result can be explained by the fact that, for an ideal solution, the contribution to the variation of thermodynamic potentials at mixing is determined exclusively by entropic effects, whereas both the entropic and energy contributions are relevant in the case of the Margules solution.

To summarize, the obtained results testify to the existence of a stabilizing effect in the entropy production; namely, the latter changes in narrower limits at a variation of the concentration gradient for the diffusing substance in comparison with the results obtained for a constant diffusion coefficient. The entropic contributions to a variation of the thermodynamic potentials at mixing play a dominant role in the change of the entropy production character in the system, whereas the account of energy contributions (the non-ideality of a solution) leads only to an insignificant quantitative variation in the entropy production.

1. S.R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962).
2. W.M. White, *Geochemistry* (Wiley-Blackwell, Oxford, Hoboken, NY, 2012).
3. V.M. Sysoev, *Fiz. Zhidk. Sost.* No. 8, 40 (1980).

4. L.A. Bulavin, D.A. Gavryushenko, V.M. Sysoev, and K.V. Cherevko, *Dopov. Nats. Akad. Nauk Ukr.*, No. 7, 67 (2012).
5. L.A. Bulavin, D.A. Gavryushenko, V.M. Sysoev, and K.V. Cherevko, *Dopov. Nats. Akad. Nauk Ukr.*, No. 12, 70 (2012).
6. B.A. Wittenberg, J.B. Wittenberg, and P.R.B. Caldwell, *J. Biol. Chem.* **250**, 9038 (1975).
7. V.M. Sysoev, I.A. Fakhretdinov, and S.G. Shpyrko, *Zh. Fiz. Khim.* **71**, 2142 (1997).
8. V.A. Durov and E.P. Ageev, *Thermodynamic Theory of Solutions* (Moscow State University, Moscow, 1987) (in Russian).

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ВИРОБЛЕННЯ ЕНТРОПІЇ В ПРОЦЕСІ ДИФУЗІЇ В ПЛОСКОПАРАЛЕЛЬНІЙ ПОРІ У ВИПАДКУ РОЗЧИНУ МАРГУЛЕСА

Резюме

У роботі отримано вираз для виробництва ентропії у випадку полегшеної дифузії бінарного розчину Маргулеса. Показано, що для вироблення ентропії існує стабілізуючий ефект за градієнтом концентрації розчину. З'ясовано, що ентропійні внески в зміну термодинамічних потенціалів при змінюванні відіграють домінуючу роль в зміні характеру вироблення ентропії в системі.