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**ENTROPY PRODUCTION BY THE DIFFUSION
 PROCESS IN A PLANE-PARALLEL PORE IN THE CASE
 OF SCATCHARD–HAMER SOLUTION**

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An expression for the entropy production in the case of facilitated diffusion in a Scatchard–Hamer binary solution has been obtained. The presence of a stabilizing effect for the entropy production with respect to the concentration gradient is shown. The entropy-driven contributions to the variation of thermodynamic potentials at the mixing are demonstrated to play the dominant role for the entropy production in the system.

Keywords: Scatchard–Hamer solution, entropy production, facilitated diffusion.

The determination of the entropy production in confined systems – such as biological membranes [1], in which chemical reactions and diffusion processes may occur (the phenomenon of facilitated diffusion), meso- and nanoobjects, and so forth – is one of the challenging problems in the thermodynamics of irreversible processes regarded as a field theory. This work aims at determining the entropy production function for a Scatchard–Hamer solution, i.e. for the solution containing at least one polar component [2], with partially miscible solutions being an example.

In work [3], the general case of entropy production by the diffusion process in the absence of external fields was considered, making allowance for chemical reactions and the gradients of a chemical potential. General expressions were obtained, which allowed the flows of diffusing substances and the entropy production in such a nonequilibrium system to be calculated.

In the case of a binary solution, when, inside a plane-parallel membrane, there are only a substratum diffusing through the membrane and a carrier that cannot go beyond the membrane boundaries (the cor-

responding thermodynamic variables are marked by subscripts 1 and 2, respectively), a system of equations for the stationary case was obtained, which allows the substratum flow J_1 to be calculated,

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

where k is the Boltzmann constant, L_1 the diagonal element in the matrix of phenomenological kinetic coefficients (the absence of nonzero nondiagonal matrix elements K_{ki} stems from the absence of vector cross-effects), v_{10} and v_{20} are the volumes of corresponding pure substances in the solution per particle, γ_1 and γ_2 are the activity coefficients of the substratum and the carrier, respectively, p is the pressure, and T is the temperature. In the case concerned, the carrier is responsible for the so-called facilitated diffusion [4], a process in which the substratum combines

with the “carrier”, and the “substratum–carrier” complex transfers the substratum through the membrane (in this case, its flow $J_2 = 0$). The system of equations (1) is supplemented with the boundary conditions,

$$\begin{cases} x_1(z=0) = x_0, \\ x_1(x=l) = x_l. \end{cases} \quad (2)$$

The corresponding entropy production is determined by the expression

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

To calculate the substance flow and the entropy production with the help of expressions (1) and (3), it is necessary to specify the dependence of the chemical potential of a solution component on the pressure, temperature, and concentration. In this work, we consider the entropy production in the framework of the proposed approach and the empirical model of Scatchard–Hamer solution, the activity coefficients for which look like [5]

$$\begin{aligned} \ln \gamma_1(T, p, x_1, x_2) = & \left(1 - \frac{v_{10}x_1}{v_{10}x_1 + v_{20}x_2} \right)^2 \times \\ & \times \left[C + 2 \frac{v_{10}x_1}{v_{10}x_1 + v_{20}x_2} \left(D \frac{v_{10}}{v_{20}} - C \right) \right], \\ \ln \gamma_2(T, p, x_1, x_2) = & \left(1 - \frac{v_{20}x_2}{v_{10}x_1 + v_{20}x_2} \right)^2 \times \\ & \times \left[D + 2 \frac{v_{20}x_2}{v_{10}x_1 + v_{20}x_2} \left(C \frac{v_{20}}{v_{10}} - D \right) \right], \end{aligned} \quad (4)$$

where $C(T, p)$ and $D(T, p)$ are dimensionless quantities depending only on solution’s temperature and pressure and characterizing the interaction between the particles of different components. In this case, the system of equations (1) can be rewritten in

the form

$$\begin{aligned} J_1 = & -2kL_1 \frac{dx_1}{dz} \times \\ & \times \left\{ \frac{1}{x_1} - 2 \frac{v_{10}v_{20}}{(v_{10}x_1 + v_{20}x_2)^2} - \left(1 - \frac{v_{10}x_1}{v_{10}x_1 + v_{20}x_2} \right) \times \right. \\ & \times \left[C + 2 \frac{v_{10}x_1}{v_{10}x_1 + v_{20}x_2} \left(D \frac{v_{10}}{v_{20}} - C \right) \right] - \\ & - \left(1 - \frac{v_{10}x_1}{v_{10}x_1 + v_{20}x_2} \right) \left(D \frac{v_{10}}{v_{20}} - C \right) \right] - \\ & - \left[v_{10} + kT \left(1 - \frac{v_{10}x_1}{v_{10}x_1 + v_{20}x_2} \right)^2 \times \right. \\ & \times \left. \left\{ \frac{\partial C}{\partial p} + 2 \frac{v_{10}x_1}{v_{10}x_1 + v_{20}x_2} \left(\frac{v_{10}}{v_{20}} \frac{\partial D}{\partial p} - \frac{\partial C}{\partial p} \right) \right\} \right] / \\ & / \left[v_{20} + kT \left(1 - \frac{v_{20}x_2}{v_{10}x_1 + v_{20}x_2} \right)^2 \times \right. \\ & \times \left. \left\{ \frac{\partial D}{\partial p} + 2 \frac{v_{20}x_2}{v_{10}x_1 + v_{20}x_2} \left(\frac{v_{20}}{v_{10}} \frac{\partial C}{\partial p} - \frac{\partial D}{\partial p} \right) \right\} \right] \times \\ & \times \left\{ 2 \frac{v_{10}v_{20}}{(v_{10}x_1 + v_{20}x_2)^2} \left(1 - \frac{v_{20}x_2}{v_{10}x_1 + v_{20}x_2} \right) \times \right. \\ & \times \left[C + 2 \frac{v_{10}x_1}{v_{10}x_1 + v_{20}x_2} \left(D \frac{v_{10}}{v_{20}} - C \right) \right] - \\ & - \left(1 - \frac{v_{20}x_2}{v_{10}x_1 + v_{20}x_2} \right) \left(C \frac{v_{20}}{v_{10}} - D \right) \right] - \frac{1}{1-x_1} \left. \right\}, \\ \frac{dx_2}{dz} = & - \frac{dx_1}{dz}, \\ \frac{dp}{dz} = & -2kT \frac{dx_1}{dz} \left\{ 2 \frac{v_{10}v_{20}}{(v_{10}x_1 + v_{20}x_2)^2} \times \right. \\ & \times \left(1 - \frac{v_{20}x_2}{v_{10}x_1 + v_{20}x_2} \right) \times \\ & \times \left[C + 2 \frac{v_{10}x_1}{v_{10}x_1 + v_{20}x_2} \left(D \frac{v_{10}}{v_{20}} - C \right) \right] - \\ & - \left(1 - \frac{v_{20}x_2}{v_{10}x_1 + v_{20}x_2} \right) \left(C \frac{v_{20}}{v_{10}} - D \right) \right] - \frac{1}{1-x_1} \left. \right\} \times \\ & \times \left[v_{20} + kT \left(1 - \frac{v_{20}x_2}{v_{10}x_1 + v_{20}x_2} \right)^2 \times \right. \\ & \times \left. \left\{ \frac{\partial D}{\partial p} + 2 \frac{v_{20}x_2}{v_{10}x_1 + v_{20}x_2} \left(\frac{v_{20}}{v_{10}} \frac{\partial C}{\partial p} - \frac{\partial D}{\partial p} \right) \right\} \right]^{-1}. \end{aligned} \quad (5)$$

The system of equations (5) together with the boundary conditions (2) completely describes the diffusion process in the membrane system if the binary solution is described by the Scatchard–Hamer model.

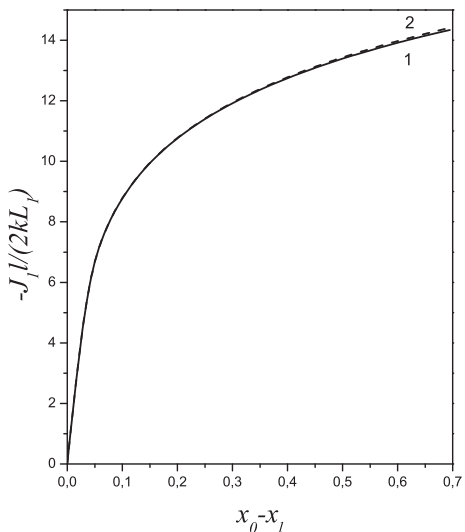


Fig. 1. Dependences of the normalized flow $-\frac{l}{2kL_1}J_1$ on the difference $x_0 - x$ in the Scatchard–Hamer solution model for various ratios $\frac{v_{10}}{v_{20}} = 0.01$ (1) and 0.5 (2). $T = 300$ K, $v_{10} = 3.8 \times 10^{-29}$ m³, $C = 2$, $D = 0.5$. At the right membrane boundary, $x_l = 5 \times 10^{-1}$

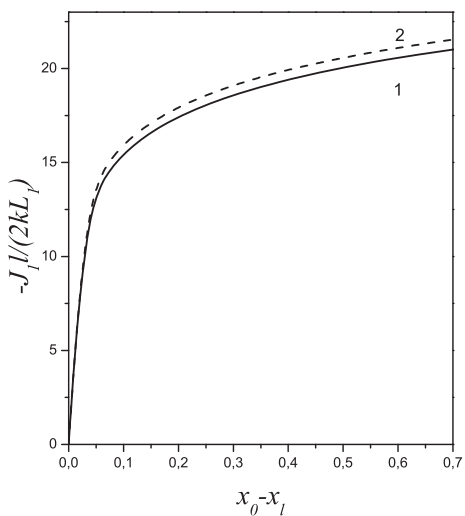


Fig. 2. The same as in Fig. 1, but for various C - and D -values: (1) $C = 2$, $D = 0.5$; (2) $C = 4$, $D = 1$. $T = 300$ K, $\frac{v_{10}}{v_{20}} = 0.01$, $v_{10} = 0.8 \times 10^{-29}$ m³. At the right membrane boundary, $x_l = 5 \times 10^{-3}$

Integrating the first equation of system (5) together with boundary conditions (2), we obtain the expression for the stationary flow J_1 ,

$$-\frac{l}{2kL_1}J_1 = 2 \ln \frac{x_l}{x_0} - A \ln \frac{1-x_l}{1-x_0} + B \ln \left| \frac{x_l - X_l}{x_0 - X_l} \right| +$$

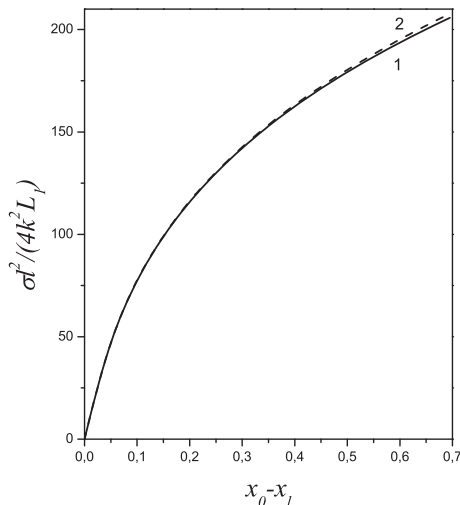


Fig. 3. Dependences of the normalized entropy production $\frac{l^2}{(2k)^2L_1}\sigma$ on the difference $x_0 - x$ in the Scatchard–Hamer solution model for various ratios $\frac{v_{10}}{v_{20}} = 0.01$ (1) and 0.5 (2). $T = 300$ K, $v_{10} = 3.8 \times 10^{-29}$ m³, $C = 2$, $D = 0.5$. At the right membrane boundary, $x_l = 5 \times 10^{-1}$

$$+ E \ln \frac{x_l + \frac{v_{20}}{v_{10}+v_{20}}}{x_0 + \frac{v_{20}}{v_{10}+v_{20}}} + F \ln \frac{x_l^2 + X_2x_l - X_3}{x_0^2 + X_2x_l - X_3} +$$

$$+ G (\arctg(X_4x_l + X_5) - \arctg(X_4x_0 + X_5)) +$$

$$+ \left\{ \left(x_l + \frac{v_{20}}{v_{10} + v_{20}} \right)^{-1} - \left(x_0 + \frac{v_{20}}{v_{10} + v_{20}} \right)^{-1} \right\} +$$

$$+ \left\{ \left(x_l + \frac{v_{20}}{v_{10} + v_{20}} \right)^{-2} - \left(x_0 + \frac{v_{20}}{v_{10} + v_{20}} \right)^{-2} \right\} +$$

$$+ \left\{ \left(x_l + \frac{v_{20}}{v_{10} + v_{20}} \right)^{-3} - \left(x_0 + \frac{v_{20}}{v_{10} + v_{20}} \right)^{-3} \right\}, \quad (6)$$

where the constants $A, B, E, F, G, H, K, R, X_1, X_2, X_3, X_4$, and X_5 are expressed in terms of the parameters for the solution and pure substance ($C, P, \frac{\partial C}{\partial p}, \frac{\partial D}{\partial p}, v_{10}$, and v_{20}). Expression (6) obtained for the stationary diffusion flow allows one, with the help of formula (3), to obtain an expression for the entropy production in the case concerned.

In Fig. 1, the dependences of the normalized substance flow diffusing through the membrane on the concentration difference between the boundaries of the system, $x_0 - x_l$, are depicted for various ratios between the partial volumes of solution components and fixed C - and D -values. Figure 2 demonstrates

the same dependences but for various C - and D -values. Figure 3 exhibits the dependences of the normalized entropy production on the concentration difference between system's boundaries $x_0 - x_l$ for various ratios between the partial volumes of components of the solution calculated for two different x_l -values and fixed C - and D -values. At last, Fig. 4 shows the dependences of the entropy production on the difference $x_0 - x_l$ for various C - and D -values.

The analysis of the presented results testifies that an almost linear dependence of the flow J_1 and an almost quadratic dependence of the entropy production σ are observed at small values of the difference $x_0 - x_l$. However, as the parameter $x_0 - x_l$ grows further, the dependence $J_1(x_0 - x_l)$ substantially deviates from a linear one, and the dependence $\sigma(x_0 - x_l)$ from the quadratic one. Moreover, a stabilizing effect is observed here: the flow and the entropy production start to weakly depend on the concentration difference between system's boundaries. The depicted results testify that, if the ratio between the partial volumes of the diffusing substance and the solvent decreases, an insignificant enhancement of the stabilizing effect is observed, as the concentration difference between the membrane boundaries increases. The same effect is also observed if only the entropy-driven terms are taken into account, i.e. in the case of the perfect solution [6].

Making allowance for the energy contributions to thermodynamic potentials at the mixing in the framework of the Scatchard–Hamer solution model enables the presence of inverse chemical reactions, which are the specific feature of diffusion processes in biological systems, to be considered more adequately in comparison with the perfect solution model. Moreover, the analysis of the presented data testifies that the account for the energy contributions to thermodynamic potentials at the mixing results in that the substance flow and the entropy production begin to depend much more weakly on the partial volume ratio between pure substances than in the case of the perfect solution. This result is quite predictable, because, in the perfect case, the contribution to the change of thermodynamic potentials at the mixing is governed exclusively by entropic effects, whereas, in the case of the Scatchard–Hamer solution, by both entropic and energy ones, with the latter obscuring the contribution of purely entropic factors. Note that the results obtained in this work on the facilitated diffusion are

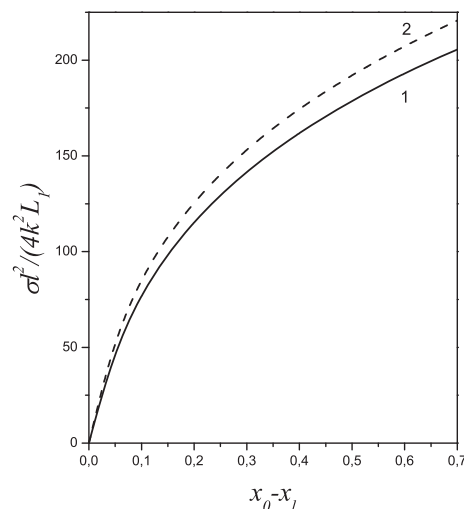


Fig. 4. The same as in Fig. 3, but for various C - and D -values: (1) $C = 2$, $D = 0.5$; (2) $C = 4$, $D = 1$. $T = 300$ K, $\frac{v_{10}}{v_{20}} = 0.01$, $v_{10} = 0.8 \times 10^{-29}$ m³. At the right membrane boundary, $x_l = 5 \times 10^{-3}$

in qualitative correspondence with both experimental results on the facilitated diffusion of biologically active substances and theoretical results obtained taking the inverse chemical reaction into account explicitly [7].

It is important to emphasize that the essential modification in the entropy production in comparison with the classical results obtained under the assumption of a constant diffusion coefficient or in the absence of chemical reactions is also typical of solutions described by the Margules model [8]. In that case, the account for energy contributions only makes the dependence of the entropy production on the partial volume ratio between pure substances smoother (i.e. purely entropic effects), but does not change the character of this dependence considerably.

Conclusions

The results obtained in this work for nonideal solutions described by the Scatchard–Hamer model testify to the existence of a stabilizing effect in the entropy production in the course of the facilitated diffusion. This effect varies within narrower limits if the gradient of the diffusing substance concentration changes, in comparison with the results obtained for the constant diffusion coefficient. The entropic contributions to the change of thermodynamic potentials at the mixing play a dominating role in the modifi-

cation of the character of an entropy production in the system, whereas the account for energy contributions (nonideality of the solution) gives rise only to insignificant quantitative variations in the entropy production.

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ПРОДУКУВАННЯ ЕНТРОПІЇ В ПРОЦЕСІ
ДИФУЗІЇ В ПЛОСКОПАРАЛЕЛЬНІЙ ПОРІ
У ВИПАДКУ РОЗЧИНУ СКЕТЧАРДА-ХАМЕРА

Резюме

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