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# Differential Phenomenological Equations of Mass Transfer of Molecular Solutions Through the Membrane

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Differential phenomenological equations of mass transfer of molecular solutions for baromembrane process are developed and discussed.

*Keywords:* Membrane process; baromembrane; mass transfer; molecular solutions; phenomenological equations

## INTRODUCTION

The main models of the baromembrane process assume the equation of flow, based on the Phenomenological irreversible processes and Gibbs-Dugem equation, which postulates that the driving force of all possible mechanisms of transfer of the components of solution through the membrane is the gradient of the chemical potential. The equation correlating the flows of the components is found and the effect of partial osmotic pressures on the correlation mechanism is discussed. The criterion of the indivisibility of the components in the

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baromembrane processes is established and it is shown that in a stationary system the decrease of the pressure on the membrane is a linear function of the transfer coordinate.

## THEORY

In the base of the Phenomenological description of the baromembrane process lies the equation of the flow, which is determinative. Therefore, we readily note the discrepancies between the three most common models of the baromembrane process.

In the diffusion model [1, 2] the initial equation of the flow  $J_i$  of the components may be shown as:

$$J_i = -(D_i/RT)c_i\nabla\mu_i \quad (1)$$

where  $D_i$  – coefficient of the diffusion,  $\mu_i$  = chemical potential,  $c_i$  – molar-volume concentration of the  $i$  component in one-dimensional approach the operator  $\nabla = \partial/\partial x$ , where  $x$  – the coordinate of the transfer on the perpendicular to the surface of the membrane.

In the frictional model [3 – 5] the initial equations are presented through the rate  $u$  of the transfer of the components (for binary system):

$$f_{ij}(u_i - u_j) + f_i u_i = -\nabla\mu_i, \quad i = 1, 2 \quad (2)$$

Here:  $f_i$  – frictional coefficient between the moving component and unmovable membrane;  $f_{ij}$  – frictional coefficient between the moving with different velocities  $i$ - and  $j$ -components according to the principle of the microscopic reversibility  $f_{ij} = f_{ji}$  at  $i \neq j$ .

In the last version of the model [6], which is found on the phenomenology of the thermodynamics of the irreversible processes, the flows for binary system are determined by the equation:

$$J_i = -L_{ii}\nabla\mu_i - L_{ij}\nabla\mu_j \quad (3)$$

in which  $L_{ij}$  – the coefficients of transfer which connected by relationship of the reciprocity of Onzager:  $L_{ij} = L_{ji}$  at  $i \neq j$ .

All of the present models assume as the driving force of the baromembrane process the gradient of the chemical potential, but the first two are determined by the flow rate  $u_i$  of the transfer, because,  $J_i = u_i c_i$ , while the third one depends directly on the flows  $J_i$ . The last

determination leads to two contradictory results. Let's simplify (3) and neglect the cross compounds of the flows and accepting  $L_{ij} = L_{ji} = 0$  at  $i \neq j$ . Expressing the chemical potential  $\mu_j$  as the function of the pressure  $P$  and the activity  $a_i$  of the component at  $T = \text{const.}$  we have.

$$J_i = -L_i \nabla \mu_i = -L_i (v_i \nabla P + RT \ln a_i), \quad (4)$$

where  $v_i$  – partial-molar volume. At  $\nabla P = 0$  from the Eq. (4) in combination with the equation

$$\partial c_i / \partial t = -\nabla (c_i u_i) = -\nabla J_i \quad (5)$$

it follows  $\partial c_i / \partial t = L_i RT \partial^2 \ln a_i / \partial x^2$ . Even at simplifying substitution of  $a$  to  $c$  this relationship is not Fick's equation.

At the absence of the division of components all the  $\nabla \ln a_i = 0$ . From (4) follows, that in this case the flow  $J_i = -L_i v_i \nabla P$  is not dependent from the concentration of the component, although must be directly proportional to it.

In the Eqs. (1) and (2) of the dissolution-diffusion and friction models the indicated contradictions are absent.

The next problem is the account of the interaction of the flows. According to [6] the Eq. (1) of the dissolution-diffusion model assume the independent mechanism of diffusion of the components through the membrane and do not account for the interaction of the flows.

On the contrary Eqs. (2) and (3) of the models of friction and the thermodynamic irreversible processes introduce the interaction of the flows with means of the cross constituents like  $f_{ij}(u_i - u_j)$  and  $L_{ij} \nabla m_j$ . However as chemical potentials of the components of the solution are connected with Gibbs-Dugem equation

$$\sum_i c_i \nabla \mu_i(P, T) = \sum_i c_i \nabla \ln a_i = 0, \quad (6)$$

the flows of components, appear to be bonded to each other (this bond will be shown below), even if they are determined by the Eq. (1). To determine whether additional bonds are necessary here, let us examine the cross constituents of the friction by putting in (2)  $f_i = 0$ . Note that in (2) the remaining members  $f_{12}(u_1 - u_2)$ ,  $f_{21}(u_1 - u_2)$  must describe the mutual diffusion of the components without the membrane. As it is seen, the given system of the equations at condition  $f_{12} = f_{21}$  requires the equity  $\nabla \mu_1 = -\nabla \mu_2$ , that contradicts the Gibbs-Dugem equation.

The analysis allows to accept as a determinative equation of the flow the expression ( $T = \text{const.}$ )

$$J_i = -(L_i/RT)c_i\nabla\mu_i, \quad (7)$$

in which the coefficient of the transfer  $L_i$  has the dimension of the diffusion coefficient. However, in  $L_i$  may be included not only the molecular-diffusion mechanism of the transfer, but also other possibilities, for example the mechanisms of the capillary and viscosity. The driving force all of the mechanisms of the transfer is the gradient of the chemical potential. Therefore the Eq. (7) should be considered as the Phenomenological equation of thermodynamics of the irreversible processes, in which the physical sense and numeral meaning  $L_i$  is determined by the participation and the partial contribution of all possible mechanisms of the transfer of the components through the membrane.

In the isothermal system at the absence of other acting external parameters except the pressure, the Eq. (7) gets the appearance:

$$J_i = -L_i c_i (v_i \nabla P + RT \nabla \ln a_i) / RT, \quad (8)$$

At the analysis of (8) and particularly at its integration another problem arises. Is it necessary to consider the membrane material or membrane itself as the component of the system and how to connect the factors  $c_i$ ,  $v_i$ ,  $a_i$  in the membrane with the same factors in the solution outside the membrane. In accordance with the initial Eqs. (7) and (8) let us inspect two aspects of the problem.

Firstly, if the membrane is considered as the component of the system we may write the equation of the flow  $J_m$ , similar to (8):

$$J_m = L_m c_m (v_m \nabla P + RT \nabla \ln a_m) / RT, \quad (9)$$

Obviously,  $J_m = 0$ , but to assume that in this case  $L_m = 0$  is physically not justified. Indeed,  $J_m = 0$  because  $\nabla P = 0$ ; membrane leaning on the inset is at the same to the pressure of the which is equal pressure of initial solution. Hence it appears that  $\nabla \ln a_m = 0$ .

Secondly, initial equation of the mass transfer (7) obviously supposes the absence of the chemical polarization, which is connected with braking of the processes by the stage of passage of the

components through the interface boundaries. So on the interface boundaries the chemical equilibrium is supposed the necessary condition of which and its conservation at variation of the parameters of the system is not only equity of the chemical potentials in the solution ( $\mu_i$ ) and in the membrane ( $\mu_{im}$ ), but also their increments:  $\mu_i = \mu_{im}$ ,  $\nabla\mu_i = \nabla\mu_{im}$ . This allows in the initial Eq. (7) to consider  $\nabla\mu_i$  as the gradient of chemical potential, which is continued into the membrane, and is occupying its free volume. Last circumstance is substantial, because in the kinetic Eq. (7), if there is no special reason amount  $c_i$  is determined in relation to all volume of the system, that is membrane.

Denoting it through  $c_{im}$  we have  $c_{im} = n_{im}/V$ , where  $n_{im}$  – number of moles of the component in the whole volume of the membrane. Introducing the porosity and free volume  $V_0$  of the membrane relation  $s = V_0/V$ , we obtain  $c_{im} = n_{im}s/V_0$ . Because  $n_{im}/V_0 = c_i$  is molar-volume concentration of the component in the free volume of membrane. Thus  $c_{im} = c_i s$  and therefore, if in (7) under  $c_i$  is understood  $c_{im} = n_{im}/V$ , then  $L_i = L_{im}$  is the real coefficient of transfer, which characterizes the entire membrane as the system. But it is possible to understand under  $c_i$  the  $c_{im} = n_{im}/V_0$ . Then  $L_i = L_{im}s$  is a coefficient of transfer, which is induced to free volume of membrane. Thus the membrane is present in the kinetic equation only as a factor determining the coefficient of transfer  $L_i$  through the real  $L_{im}$  and porosity  $s$ :

$$L_i = L_{im}s \quad (10)$$

The effects of interaction of the membrane material and the components of solution are reflected only through  $L_{im}$ , while the membrane porosity, introduced by the relation  $s = V_0/V$ , may not coincide with the porosity, determined experimentally by the known standard methods, although it should be close to it.

Hence, the two described aspect allow as correctly, as the primary kinetic equation is correct (7) to exclude the membrane as the component of the system, implying  $c_i$ ,  $v_i$  and  $a_i$  as variable of the solution, extended into the membrane and occupying its free space.

Finally we shall note, that the solution of the proposed problem through the law of distribution of components between the membrane and the solution as  $K_i = a_{im}/a_i$  in this case is seeming. Really, taking the

Gibbs-Duhem equation for two dissolved components and the membrane material

$$c_{1m}d \ln a_{1m} + c_{2m}d \ln a_{2m} + c_m d \ln a_m = 0, \quad (11)$$

we have for the membrane material  $d \ln a_{2m} = 0$ , and for dissolved components  $d \ln a_{1m} = d \ln a_1$ , because  $d \ln a_{2m} = d \ln a_2$ . We can then express the distribution law as

$$K_i = \gamma_{im} N_{im} / \gamma_i N_i = \gamma_{im} c_{im} (c_1 + c_2) / \gamma_i c_i (c_{1m} + c_{2m} + c_m)$$

where  $\gamma$  and  $N$  – corresponding coefficients of activity and mole parts. By inserting  $c_{im} = K_i \gamma_i c_i (c_{1m} + c_{2m} + c_m) / \gamma_i (c_1 + c_2)$  we obtain as alternative of (11)

$$K_1 (\gamma_1 / \gamma_{1m}) c_1 d \ln a_1 + K_2 (\gamma_2 / \gamma_{2m}) c_2 d \ln a_2 = 0 \quad (12)$$

Comparing (12) with the Gibbs-Duhem equation for double solution, we get the equation  $K_1 (\gamma_1 / \gamma_{1m}) = K_2 (\gamma_2 / \gamma_{2m})$ , which does not add anything new to the problem under study.

Let us determine and analyze the main consequences of (8).

1. If we divide  $J_i$  on  $L_i$  and sum the left and right parts of (8) on all the components of the solution taking into account the Gibbs-Duhem Eq. (6) and correlations  $\sum_i c_i v_i = \sum_i \phi_i = 1$ , in which  $\phi_i = c_i v_i$  – volume part, we shall get the equation of connection between the flows

$$\sum_i J_i / L_i = -\nabla P / RT. \quad (13)$$

In particular case  $\nabla P = 0$  the Eq. (13) determines the connection between the flows at co-diffusion of the components. For binary solution

$$J_1 / L_1 + J_2 / L_2 = -\nabla P / RT \quad (14)$$

Here we see, that effect of admixtures of the slow component to fast component increases with decreasing the transfer coefficient  $L_2$  of the slow component and higher its concentration, correspondingly flow  $J_2$ . Therefore, the fast component flow is changed proportion-

ally to  $L_1$ , and slow one to  $L_2$ , because  $L_1 > L_2$ . Thus, the increase of slow component concentration the volume flow decreases, that is the efficiency of baromembrane process decreases. The hermetically sealing role of the admixtures, for instance of antifreeze in the system of engine cooling, represents not only a physical sealing of the pores, but also in abrupt decrease of the quick component flow due to relation (14). The mechanism of this relation consists in that the separation of the components in the baromembrane process creates forces counteracting this separation. Therefore, it is convenient to consider them in terms of the osmotic pressure forces.

From definition of the osmotic pressure

$$\Pi_i = -RT \int_1^{a_i} d(\ln a_i)/v_i$$

follows

$$\nabla_i \Pi = -(RT/v_i) \nabla \ln a_i \quad (15)$$

Using (15), we can change the Eq. (8)

$$J_i = -(L_i/RT) \phi_i (\nabla P - \nabla \Pi_i), \quad (16)$$

The Eq. (16) differs from that presented in (7) and needs the artificial introduction of the reflectance coefficient. According to (15) and (16), the partial osmotic pressures, appearing at accelerating the movement of the slow component, prevents their separation.

2. If the  $c$  of the component lowering the flow of the fast composition of the solution does not change in the baromembrane process, all of the  $\nabla \ln a_i = 0$ . As by this  $J_i/J_j = c_i/c_j$  the condition of the indivisibility of the components of the binary solution, according to (8) demands the equality

$$L_i v_i = \text{const.} \quad (17)$$

Divisibility of the components in the baromembrane process is possible only at condition  $L_i v_i = L_j v_j$  while the fast component is that having a higher  $L_i v_i$ . This circumstance, that the correlation



- between  $L_i v_i$ , but not  $L_i$ , is the factor of separation of the components of the binary solution, allows us to explain experimentally the observed cases, when high-molecular compounds appear to be more permeable for the membrane, than the low-molecular components. Really, if the molecular mass of the compound, and correspondingly its  $v_i$ , increases due to the length of the chain, but by this the transfer mechanism of the component through the membrane is similar to the movement of the snake, crawling into the borrow, than the transfer coefficient of the component may stay practically the same or decrease, but in a lesser extent, that increases  $v_i$ . As a result with the growth of the molecular mass (length of the chain) factor  $L_i v_i$  increases, increasing the mobility of the component in the membrane. For the binary solution the condition of indivisibility of components (17) demands the equality  $L_1 v_1 = L_2 v_2$ . By introducing of the third component, differing by the mobility factor from the first to second, the indivisibility of the later means  $\nabla \ln a_1 = \nabla \ln a_2 \neq 0$  and needs equalities  $L_1 = L_2$ ,  $v_1 = v_2$ . If they are not executed, the introduction of the third component makes divisible the components, which are indivisible in the binary system according to condition  $L_1 v_1 = L_2 v_2$ .
3. In the stationary system  $\partial c_i / \partial t = 0$  and  $\nabla J_i = 0$ , hence  $J_i = \text{const.}$  and is an integral of the process. That is why according to (13) in this case  $\nabla P = \text{const.}$  the decrease of pressure on the membrane is the linear function of the coordinate of transfer. Hence,

$$\nabla P = (P'' - P') / \delta_m = \Delta P / \delta_m \quad (18)$$

where  $\Delta P = P'' - P'$  – difference of pressures to ( $P'$ ) and after ( $P''$ ) membrane;  $\delta_m$  – effective thickness of the membrane.

The relationship (18) is constantly used for the integration of the differential equations of transfer for all models [1 – 6], but as limited-differential approach, but not the conclusion.

With the account of the equation of the connection between the flows (13) may be written in the integral form, which is convenient for the experimental check and calculation of the coefficients of transfer:

$$\sum_i J_i / L' = -\Delta P / RT \quad (19)$$

Here  $L'_i = L_i/\delta_m$  – effective coefficient of transfer, which is induced to the nit of thickness of the working layer of the membrane.

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