Eur Biophys J (1989) 17:137–142

European
Biophysics Journal

The Gibbs-Duhem equation in membrane transport

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Received March 8, 1988/Accepted in revised form February 20, 1989

Abstract. It is argued that the Gibbs-Duhem equation alone cannot be used for deriving conclusions about the pressure gradient in membrane permeation. Statements regarding spatial variation of pressure in conjunction with chemical potential gradients of the components can legitimately be drawn from an equation that results from a combination of the G-D equation and the mechanical equilibrium equation. The derived equation has been applied here for explaining the mechanics of osmosis. In a further application, the frictional model has been improved here because the driving force also includes the membrane-solute potential interaction, thus allowing the solute partition coefficient to appear in the calculations naturally. By recognizing that because of the membrane-solution interaction, external forces of both potential and frictional character are present, the dissipation function is shown to depend explicitly on the centre-of-mass velocity. Thus the reference velocity for diffusive fluxes cannot be chosen arbitrarily, making Prigogine's theorem invalid in this approach to describing membrane permeation.

Key words: Gibbs-Duhem equation, mechanical equilibrium, membrane permeation, pressure gradient, dissipation function

I. Introduction

Irreversible thermodynamics has been widely applied for describing membrane processes. As presented in textbooks (e.g., de Groot and Mazur 1962), the theory is very general. It copes with all transport processes that may occur in open, non-isothermal and non-isobaric systems; it describes both diffusive and viscous flows, it allows for chemical reactions and external fields that may be present in the system. However, it does need some modification when applied to membrane transport. First, it should be noticed that all interactions of a solution with the membrane should be classified as external. Thus, solute-membrane and water-membrane interaction forces should be treated as external forces, which can be of potential and/or frictional character. So in addition to external potential field forces we have to consider external friction forces in an irreversible thermodynamic treatment of membrane permeation. Second, we notice that membrane systems operate in mechanical equilibrium, whenever we restrict ourselves to membranes which, owing to their dense structure, do not allow viscous flow to occur and which are in the state of swelling equlibrium. This allows us to make considerable simplifications in the theory.

In this report we show that the above two observations have an important bearing on the mechanics of membrane transport. Besides being a thermodynamic process, membrane permeation is also a mechanical process of flow occurring usually under the condition of spatial variation of pressure. Conclusions regarding the occurrence of pressure gradients were drawn from the Gibbs-Duhem equation written in the form: $\operatorname{grad} p = \sum c_i \operatorname{grad} \mu_i$.

Expressing the chemical potential of i^{th} species as $\mu_i = \mu_i^o + \bar{V}_i p + \mu_i^c$ and putting $\sum c_i \bar{V}_i = 1$, we get the equation transformed to $\sum c_i \nabla \mu_i^c = 0$. This is the true, non-trivial content of the G-D equation, i.e. the concentration-dependent parts of chemical potentials are not independent. The G-D equation makes no statements about the occurrence of a pressure gradient. It says only that if a pressure gradient exists then it is equal to the term $\sum c_i \nabla \mu_i$. A pressure gradient is a force, and the question of its existence must involve the momentum balance equation. In mechanical equilibrium and in the absence of viscous flow this equation reduces to $\nabla p = \sum c_i \bar{f}_i^{\text{ext}}$. The external force f_i^{ext} is the membrane-species interaction force, composed of potential and frictional interactions: $\bar{f}_i^{\text{ext}} = \bar{f}_i^{\text{ext} \cdot p} + \bar{f}_i^{\text{ext} \cdot f}$. With this and putting $\nabla \mu_i - \bar{f}_i^{\text{ext} \cdot p} = \nabla \mu_i(x)$ by definition, the G-D equation together with the mechanical equilibrium equation results in $\sum c_i(\nabla \mu_i(x) - \bar{f}_i^{\mathrm{ext}\cdot f}) = 0$. Only this equation, and not the G-D equation alone, allows us to draw correct conclusions about the existence of a pressure gradient in conjunction with chemical potential gradients of the components. This equation has already been applied by the present author for explaining the mechanism of osmosis (Tomicki 1978a, b) and capillary osmosis (Tomicki 1985).

In the present work we give a deeper theoretical justification for the proposed approach and further examples of its application. First by treating the equilibrium between permeant within and outside the membrane as an interface equilibrium we incorporate the approach in the formalism of equilibrium thermodynamics. Then we also incorporate it in the irreversible thermodynamic description.

The introduction of external forces of friction (in addition to potential ones usually present in irreversible thermodynamic treatments) makes diffusive entropy production explicitly dependent on the centre-of-mass velocity. This velocity cannot, therefore, be replaced by any other reference velocity in the definition of diffusional fluxes. Hence Prigogine's theorem does not hold for this way of describing membrane permeation. The useful results of the present treatment are derived for diffusive type of flow. Therefore they are applicable to membranes within which viscous flow cannot develop, which I think is the normal situation, especially in biological membranes.

II. Equilibrium between the membrane and the bathing solution as an interphase equilibrium and the Gibbs-Duhem equation

In order to successfully describe membrane phenomena, first we have to have a means by which the thermodynamic state of the permeating solution can be described both inside and outside the membrane. The solution outside is a free solution and it can be well described by the well-known thermodynamics of free solution. The solution within, however, being in direct and close contact with the membrane matrix, is definitely not free. It has to share not only space with the membrane, but its thermodynamic characteristics are altered owing to forces of interaction between the solution and membrane. A hydrophilic membrane matrix lowers the potential energy of water molecules which are in close contact with the matrix. It also affects water structure and thus the whole solution. The resultant effect is a changed free energy density of the matrix-bound solution as compared to that of the free solution outside the membrane. Thus we can legitimately talk of two phases: one being the solution inside the membrane and the other the solution outside the membrane. Treating the solution within the membrane and the solution outside the membrane as a two-phase system we account for all equilibrium membrane-solution interaction and thermodynamically nothing else matters. The fact that the solution within the membrane does not occupy the whole geometrical space but only that fraction which is left free by the membrane matrix has no thermodynamic significance, provided we refer all state parameters to that solution-occupied fraction of space.

The solution-membrane interaction may of course vary from place to place within the membrane because the membrane may not be homogeneous. Even if it is homogeneous we find a very strong position dependence of the interaction throughout the interphase boundary when treated as a layer of finite thickness with continuous profiles of all the parameters. Space variation of the interaction brings about gradients of thermodynamic state functions. Thus, for instance, a gradient of the Gibbs free energy density of the solution can occur, implying the existence of an external force on the solution, which of course can only be the membrane-solution interaction force. The existence of external forces means that the system can exchange energy with the surroundings in the form of work, other than the expansion work, $p\,\mathrm{d}V$. We are concerned here with situations when the system is allowed to perform work at the expense of its own energy, and not when the external force performs work on the system. Therefore the work term in the first law of thermodynamics must be taken with the minus sign. Allowing also for the second law we have for the state of thermodynamic equilibrium the equation (Gumiński 1964):

$$\delta U - T\delta S + p\delta V + \delta W = 0 \tag{1}$$

The "δ" sign means virtual (imagined) variations of the respective quantities, as in the state of thermodynamic equilibrium they in fact do not change. In terms of the Gibbs free energy $G = U - TS + pV$ and for constant temperature and pressure, Eq. (1) reads:

$$\delta G = -\delta W \tag{2}$$

We now apply this general equilibrium condition to our membrane-bound solution. Assuming that the membrane-solution interaction may vary continuously in space, we have in fact a continuous transition from one phase to another. To avoid undue mathematical complications, we chose a system which is non-homogeneous in one direction only, i.e. in the x-direction, and consider a bar of length d and unit cross-section aligned with the x axis, which begins where the homogenous phase (′) ends and ends were the homogeneous phase (″) begins. The total free energy of the bar can be expressed as

$$G = \int_0^d g(x)\,\mathrm{d}x \tag{3}$$

where the volume density of free energy is $g(x) = g(T, p, n_i, x)$, i.e. is a function of temperature, pressure, number of moles of each species and of position x. So the variation of $g(x)$ at constant T and p is given by

$$\delta g(x) = \sum^{\alpha} \frac{\partial g(x)}{\partial n_i} \delta n_i + \frac{\partial g(x)}{\partial x} \delta x \tag{4}$$

Since $g(x) = \mathrm{d}G(x)/\mathrm{d}x$ and $\partial g(x)/\partial x = -f^{\text{ext}}$,

$$\delta g(x) = \sum^{\alpha} \frac{\mathrm{d}}{\mathrm{d}x}\left[\frac{\partial G(x)}{\partial n_i}\right] \delta n_i - f(x)\,\delta x \tag{5}$$

By definition $(\partial G(x)/\partial n_i)_{T,p,n_{j \neq i}} = \mu_i(x)$ is the augmented chemical potential of the i^{th} species. By virtue of Eq. (2) we obtain:

$$\int_0^d \left(\sum^{\alpha} \frac{\mathrm{d}\mu_i}{\mathrm{d}x} \delta n_i - f(x)\,\delta x\right) \mathrm{d}x = -\int_0^d f(x)\,\delta x\,\mathrm{d}x \tag{6}$$

As δn_i are variations of physically independent components, it is possible to transfer from phase to phase only any one of them at a time. Putting $\delta n_i \neq 0$ and $\delta n_{j \neq i} = 0$, we get from Eq. (6) $\mathrm{d}\mu_i = 0$ meaning that $\mu_i' = \mu_i''$. These are independent equations that should hold for thermodynamic equilibrium of the two phases. However, the system is also in mechanical equilibrium and therefore an additional condition must hold, i.e.:

$$\nabla p = \bar{f}^{\text{ext}}(x) \tag{7}$$

On integration, this requires that $p'' - p' = \int_0^d f(x)\,\mathrm{d}x$. This mechanical equilibrium equation together with the α equations expressing thermodynamic equilibrium give us $\alpha + 1$ equations imposed on the system. The number of independent intensive parameters of the system is: $2(\alpha - 1)$ concentrations, two pressures and one temperature. Subtracting the number of equations from the number of parameters we find that the number of degrees of freedom $s = \alpha$. This result is in accord with the Gibbs phase rule saying that $s = \alpha - \beta + 2$, as β equals two in our case.

By definition of G and the first law of thermodynamics we have for volume density of free energy the expression:

$$\mathrm{d}g(x) = -s\,\mathrm{d}T + \mathrm{d}p + \sum \mu_i(x)\,\mathrm{d}c_i - f^{\text{ext}\cdot p}(x)\,\mathrm{d}x \tag{8}$$

On the other hand, $g(x)$ can be expressed by the partial quantities $\mu_i(x)$ as follows: $g(x) = \sum c_i \mu_i(x)$. The differential of this when compared with (8) gives us

$$\mathrm{d}p = \sum c_i\,\mathrm{d}\mu_i(x) + f^{\text{ext}\cdot p}\,\mathrm{d}x \tag{9}$$

This when combined with the mechanical equilibrium equation (7) results in

$$\sum c_i \nabla \mu_i(x) = 0 \tag{10}$$

This equation corresponds to the Gibbs-Duhem equation for the thermodynamics of free solution: $\sum c_i \nabla \mu_i = \nabla p$. In order to find a relationship between the two equations, we have to have correlation between $\mu_i(x)$ and μ_i. Our membrane-bound solution can be regarded as free solution when we leave aside the mechanical energy. Then the normal chemical potentials describe the system and the Gibbs-Duhem equation holds. Allowing also for the mechanical equilibrium condition: $\nabla p = \sum c_i \bar{f}_i^{\text{ext}\cdot p}$, we get

$$\sum c_i (\nabla \mu_i - \bar{f}_i^{\text{ext}\cdot p}) = 0 \tag{11}$$

Comparing (10) with (11) we see that $\nabla \mu_i(x) = \nabla \mu_i - \bar{f}_i^{\text{ext}}$. Now by definition we put $\nabla \mu_i^E = -\bar{f}_i^{\text{ext}\cdot p}$. So, $\nabla \mu_i(x) = \nabla(\mu_i + \mu_i^E)$ and thus $\mu_i(x) = \mu_i + \mu_i^E = \mu_i^o + \bar{V}_i p + \mu_i^c + \mu_i^E$, where μ_i^c is the concentration-dependent part and μ_i^E is an excess part of the augmented chemical potential $\mu_i(x)$. It represents the total mechano-thermodynamic potential of a mixture component, and thus $-\nabla \mu_i(x)$ is the total driving force on the component. In the stationary state this force must be balanced by the total force of friction:

$$\bar{f}_i^f - \nabla \mu_i(x) = 0 \tag{12}$$

This we multiply by c_i and sum.

$$\sum c_i (\bar{f}_i^{\text{ext}\cdot f} + \bar{f}_i^{\text{int}\cdot f}) - \sum c_i \nabla \mu_i(x) = 0 \tag{13}$$

As the forces of internal friction add up to zero, we obtain

$$\sum c_i (\nabla \mu_i(x) - \bar{f}_i^{\text{ext}\cdot f}) = 0 \tag{14}$$

As mentioned in the introduction, this equation results also from trivial combination of the Gibbs-Duhem equation and the mechanical equilibrium equation. Now we see that such trivial derivation can be thermodynamically corroborated when the free energy and thus also the internal energy functions are augmented with the potential energy of the membrane-solution interaction.

Using the relation between $\mu_i(x)$ and μ_i, and the mechanical equilibrium condition, one can easily see that Eq. (10) is compatible with the G-D equation.

III. Irreversible thermodynamics for membrane permeation

We now incorporate Eq. (14) in the formalism of irreversible thermodynamics. The starting point is the momentum balance equation for a solution permeating through a membrane:

$$\varrho \frac{\mathrm{d}\bar{v}}{\mathrm{d}t} = -\mathrm{Div}\hat{\pi} + \sum \varrho_i (\bar{f}_i^{\text{ext}\cdot p} + \bar{f}_i^{\text{ext}\cdot f}) \tag{15}$$

All forces in this section are forces per mass unit although denoted in the same way as forces per mole of the previous section. This equation differs from that used in standard treatments in that it contains external forces of friction $f_i^{\mathrm{ext}\cdot f}$ besides those of potential field forces $f_i^{\mathrm{ext}\cdot p}$. By standard procedures (Baranowski 1974) we can obtain from Eq. (15) the kinetic energy source term of the form (neglecting the kinetic energy of diffusion):

$$\sigma_k = \hat{\pi}:\mathrm{Grad}\,\bar{v} + \bar{v}\sum\varrho_i(\bar{f}_i^{\mathrm{ext}\cdot f} + \bar{f}_i^{\mathrm{ext}\cdot p}) \tag{16}$$

The potential energy source term has the form: $\sigma_p = -\sum\varrho_i\bar{v}_i\bar{f}_i^{\mathrm{ext}\cdot p}$. Because of the energy conservation law, we have the following balance equation for total energy per unit mass:

$$\frac{\partial\varrho e}{\partial t} = -\mathrm{div}\,\bar{I}_{\varrho e} \tag{17}$$

Total energy is composed of kinetic, potential and internal energy and its source term is equal to zero:

$$\sigma_e = \sigma_k + \sigma_\varphi + \sigma_u = 0 \tag{18}$$

Hence $\sigma_u = -\sigma_k - \sigma_\varphi$. Having the source terms of kinetic and potential energy calculated, we can obtain (after dropping the viscous dissipation term in $\hat{\pi}:\mathrm{Grad}\,\bar{v} = p\,\mathrm{div}\,\bar{v} + \hat{\pi}_{\mathrm{visc}}:\mathrm{Grad}\,\bar{v}$)

$$\sigma_{\varphi u} = -p\,\mathrm{div}\,\bar{v} + \sum\bar{I}_i^d\,\bar{f}_i^{\mathrm{ext}\cdot p} - \bar{v}\sum\varrho_i\,\bar{f}_i^{\mathrm{ext}\cdot f} \tag{19}$$

where $\bar{I}_i^d = \varrho_i(\bar{v}_i - \bar{v})$ is the diffusion flux. Expression (19) tells us that internal energy can emerge or disappear as a result of the work done during expansion or compression of a volume element (first term), as a result of work done by potential membrane-solution interaction (second term) and as a result of friction between the membrane and permeating solution. It is worth noting that the frictional contribution is always positive, because the resultant of the forces of friction is in the opposite direction to the centre-of-mass velocity v. The internal energy conforms to the balance equation:

$$\frac{\partial\varrho u}{\partial t} = -\mathrm{div}(\varrho u\bar{v} + \bar{I}_q) + \sigma_{\varrho u} \tag{20}$$

where I_q is the total heat flux. With (19) and the mass continuity equation we can transform Eq. (20) to

$$\varrho\frac{\mathrm{d}u}{\mathrm{d}t} = -\mathrm{div}\,\bar{I}_q - p\,\mathrm{div}\,\bar{v} + \sum\bar{I}_i^d\,\bar{f}_i^{\mathrm{ext}\cdot p} - \bar{v}\sum\varrho_i\,\bar{f}_i^{\mathrm{ext}\cdot p} \tag{21}$$

Using the mass continuity equation one can get $\mathrm{div}\,\bar{v} = \varrho\,\mathrm{d}\bar{V}/\mathrm{d}t$, where $\bar{V} = \varrho^{-1}$ is the specific volume. Now the basic Gibbs equation is employed.

$$T\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{\mathrm{d}u}{\mathrm{d}t} + p\frac{\mathrm{d}\bar{V}}{\mathrm{d}t} - \sum\bar{\mu}_i\frac{\mathrm{d}y_i}{\mathrm{d}t} \tag{22}$$

where s is specific entropy (per unit mass), $\bar{\mu}_i$ is chemical potential and y_i – mass fraction. Using again the mass balance we can find that $\mathrm{d}y/\mathrm{d}t = -\bar{V}\,\mathrm{div}\,\bar{I}_i^d$.

Now, with (21) the Gibbs equation can be rewritten as

$$\varrho T\frac{\mathrm{d}s}{\mathrm{d}t} = -\mathrm{div}\,\bar{I}_q + \sum\bar{I}_i^d\,\bar{f}_i^{\mathrm{ext}\cdot p} - \bar{v}\sum\varrho_i\,\bar{f}_i^{\mathrm{ext}\cdot f} + \sum\bar{\mu}_i\,\mathrm{div}\,I_i^d \tag{23}$$

Following standard procedures (Baranowski 1974), and using the balance equation for entropy one can find the entropy source term and thus the dissipation function of the form:

$$\sigma T = \bar{I}_q^d\,\bar{X}_q + \sum I_i^d\,\bar{X}_i - \bar{v}\sum\varrho_i\,\bar{f}_i^{\mathrm{ext}\cdot f} \tag{24}$$

where $\bar{I}_q^d$ is the flux of conducted heat relative to the centre-of-mass velocity $\bar{v}$, and $\bar{X}_q = -\nabla T/T$ – the corresponding force; $\bar{I}_i^d = \varrho_i(\bar{v}_i - \bar{v})$ is the diffusion flux and $\bar{X}_i = -(\nabla\bar{\mu}_i)_T + f_i^{\mathrm{ext}\cdot p}$ – the corresponding force.

The form of the dissipation function (24) stays the same when we convert from kilograms to moles. This can be easily done by using the relations: $\varrho_i = c_i M_i$ and $\bar{\mu}_i = \mu_i/M_i$. So now we return to the previous convention when $\bar{I}_i^d = c_i(\bar{v}_i - \bar{v})$ and $\bar{X}_i = -(\nabla\mu_i)_T + \bar{f}_i^{\mathrm{ext}\cdot p}$, i.e. molar fluxes and forces per mole.

The obtained energy dissipation function depends explicitly on the external forces of friction and the centre-of-mass velocity. That dependence can be lifted by transforming the fluxes to the laboratory frame of reference and using the G-D equation together with the mechanical equilibrium condition. The result, for isothermal systems, is:

$$\sigma_d T = \sum\bar{I}_i\bar{X}_i \tag{25}$$

where $I_i = c_i v_i$ are diffusive fluxes relative to the membrane. In view of the explicit dependence of the dissipation function (24) on the reference velocity $\bar{v}$ for diffusive fluxes, that velocity cannot be chosen arbitrarily. In fact, Prigogine's theorem cannot hold because we find that

$$-\sum c_i\bar{X}_i = \sum c_i\,\bar{f}_i^{\mathrm{ext}\cdot f} \tag{26}$$

and not zero as conformity with that theorem would require. Introducing the augmented chemical potential $\mu_i(x) = \mu_i + \mu_i^E$ to (26) we obtain Eq. (14) yet again.

IV. Examples of application

a) *Osmosis*

In osmosis water flows from lower to higher pressure regions, performing work against external forces at the expense of the free energy of the solution. The mechanism of this simple phenomenon has been the matter of controversy (e.g., Soodak and Iberall 1979). The usual thermodynamic treatment of osmosis is in terms of the chemical potential difference of water on both sides of the membrane. In this way, it specifies the energy available for the flow. However, it says nothing about the mechanics of the phenomenon, and thus about the force which drives water against its pressure gradient and the forces of friction. Our Eq. (14) resolves the problem immediately. In an osmotic system the forces of external friction are those between the membrane and the solution components. Thus Eq. (14) gives us:

$$c_s \operatorname{grad} \mu_s(x) - c_s \bar{f}^f_{sm} + c_w \operatorname{grad} \mu_w(x) - c_w \bar{f}^f_{wm} = 0 \tag{27}$$

Taking into account that $\mu_i(x) = \mu_i^o + \bar{V}_i p + \mu_i^E + \mu_i^c$ and $\sum c_i \operatorname{grad} \mu_i^c = 0$, we obtain:

$$c_s \bar{f}_{sm} + c_w \bar{f}^f_{wm} - c_w \nabla \mu_w^E - \nabla p = 0 \tag{28}$$

where $\bar{f}_{sm} = \bar{f}^f_{sm} - \operatorname{grad} \mu_s^E$ is the total force of solute-membrane interaction. Equation (28) explains osmosis by saying that the solute-membrane interaction force drives water against the pressure gradient and the force of water-membrane interaction.

In osmotic equilibrium $f^f_{wm} = 0$ because water does not flow through the membrane. If the membrane is ideally semi-permeable, $f^f_{sm} = 0$ and Eq. (28) reduces to $-c_s \operatorname{grad} \mu_s^E - c_w \operatorname{grad} \mu_w^E = \operatorname{grad} p$. Now, as solute is in thermodynamic equilibrium, $\operatorname{grad} \mu_s(x) = 0$. The two last equations when combined give us:

$$(1 - c_s \bar{v}_s) \operatorname{grad} p = RT \operatorname{grad} c_s - c_w \operatorname{grad} \mu_w^E \tag{29}$$

where we have taken $\mu_s^c = RT \ln c_s$.

This equation we integrate across the membrane as follows (see Fig. 1).

$$\int_0^d \mathrm{d}p - \int_{x_2}^d c_s \bar{V}_s \mathrm{d}p = RT \int_0^d \mathrm{d}c_s - \int_0^d c_w \mathrm{d}\mu_w^E \tag{30}$$

$$\int_0^d c_w \mathrm{d}\mu_w^E = \left(\int_0^{x_1} + \int_{x_1}^{x_2} + \int_{x_2}^{d} \right) c_w \mathrm{d}\mu_w^E = \tag{31}$$

$$= \langle c_w \rangle [\mu_w^E(x_1) - \mu_w^E(0) + \mu_w^E(d) - \mu_w^E(x_2)] = 0$$

Putting $p(0) = 0$ and denoting by $\langle \varphi_s \rangle$ and $\langle \varphi_w \rangle$ the average volume occupied by solute and water within the active thickness from x_2 to d, we obtain:

$$\pi = \frac{1}{\langle \varphi_w \rangle} RTc_s - \frac{\langle \varphi_s \rangle}{\langle \varphi_w \rangle} p(x_2) \tag{32}$$

This result tells us that osmotic pressure is slightly larger than RTc_s ($\langle \varphi_w \rangle \approx 1$) and it depends weakly on swelling pressure $p(x_2)$ ($\langle \varphi_s \rangle / \langle \varphi_w \rangle \ll 1$).

b) The frictional model

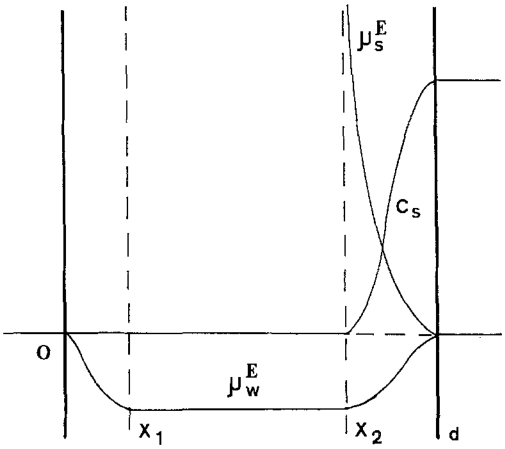

Fig. 1. Spatial variation of solute concentration, excess of its chemical potential and excess of water chemical potential within a semi-permeable membrane

As the gradient of the augmented chemical potential with the minus sign is the total driving force on a component, it must be balanced by the total force of friction on the component: $\operatorname{grad} \mu_i(x) = \bar{f}_i^f$. Thus, we can now talk in terms of the so-called frictional model, made popular by Spiegler (1958). For solute, water and membrane we thus have:

$$\operatorname{grad} \mu_s(x) = \bar{f}^f_{sm} + \bar{f}^f_{sw} \tag{33}$$

The forces of friction can be written as being proportional to the relative velocities of the components:

$$\bar{f}^f_{sm} = -f_{sm}(\bar{v}_s - \bar{v}_m), \quad \bar{f}^f_{sw} = -f_{sw}(\bar{v}_s - \bar{v}_w) \tag{34}$$

In the state of osmotic equilibrium ($v_w \approx 0$) and with the membrane chosen as the frame of reference, Eqs. (33) and (14) can thus be written:

$$c_s \operatorname{grad} \mu_s(x) = -(f_{sm} + f_{sw}) \bar{I}_s \tag{35}$$

$$c_s \operatorname{grad} \mu_s(x) + c_s \operatorname{grad} \mu_w(x) = -f_{sm} \bar{I}_s \tag{36}$$

Combining (35) with (36):

$$c_w \operatorname{grad} \mu_w(x) = f_{sw} \bar{I}_s \tag{37}$$

Integration of (35) and (37) across the membrane thickness gives:

$$\int_0^d c_s \mathrm{d}\mu_s(x) = -(f_{sn} + f_{sw}) I_s d \tag{38}$$

$$\int_0^d c_w \mathrm{d}\mu_w(x) = f_{sw} I_s d \tag{39}$$

Now the integrals on the left-hand sides of (38) and (39) can be expressed as follows:

$$\int_0^d c_s \mathrm{d}\mu_s(x) = \int_0^d c_s(\bar{V}_s \mathrm{d}p + \mathrm{d}\mu_s^E + RT \mathrm{d} \ln c_s) =$$

$$= \langle \varphi_s \rangle \Delta p + \int_0^d c_s \mathrm{d}\mu_s^E + \Delta\pi \tag{40}$$

$$\int_0^d c_w \mathrm{d}\mu_w(x) = \int_0^d c_w \left(\bar{V}_w \mathrm{d}p + \mathrm{d}\mu_w^E - RT \frac{\mathrm{d}c_s}{c_w} \right) =$$

$$= \langle \varphi_w \rangle \Delta p - \Delta\pi \tag{41}$$

because $\int_0^d c_w \mathrm{d}\mu_w^E = 0$ (see previous example).

The integral $\int_0^d c_s \mathrm{d}\mu_s^E = \Delta\pi(K_s - 1)$ as will be shown later. Using expressions (40) and (41), and combining

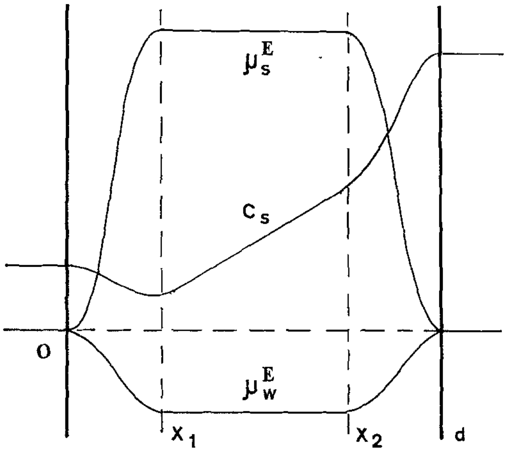

Fig. 2. Spatial variation of solute concentration, excess of its chemical potential and excess of water chemical potential within a membrane permeable to solute and water

(38) with (39), we obtain

$$\varphi_s \Delta p + K_s \Delta\pi = \frac{f_{sm} + f_{sw}}{f_{sw}} (\Delta\pi - \varphi_w \Delta p) \tag{42}$$

Introducing the reflection coefficient $\sigma = \Delta p / \Delta\pi$ into (42), we obtain after some rearrangement

$$\sigma = \frac{f_{sm} + f_{sw} - K_s f_{sw}}{\varphi_w (f_{sm} + f_{sw}) - \varphi_s f_{sw}} \tag{43}$$

Assuming the usual approximation valid for dilute solutions: $\varphi_w = 1$ and $\varphi_s = 0$,

$$\sigma = 1 - \frac{K_s f_{sw}}{f_{sm} + f_{sw}} \tag{44}$$

In order to calculate the integral $\int_0^d c_s \mathrm{d}\mu_s^E$ we assume the solute distribution at the solute-membrane physical interface to conform to the Boltzmann equilibrium distribution

$$c_s = c_s^0 \exp(-\mu_s^E(x)/RT) \tag{45}$$

which is consistent with the requirement that $\nabla \mu_s(x) = 0$. The functions $\mu_s^E(x)$ and $c_s(x)$ are like those in Fig. 2. Within a homogeneous membrane $\mu_s^E(x)$ varies only at the physical interfaces, so the integral

$$\int_0^d c_s \mathrm{d}\mu_s^E = \left(c_s^1 \int_0^{x_1} - c_s^r \int_d^{x_2} \right) \exp(-\mu_s^E/RT) \mathrm{d}\mu_s^E = \tag{46}$$
$$= RTc_s^1(1-K_s) + RTc_s^r(K_s - 1) = \Delta\pi(K_s - 1)$$

where $K_s = c_s^{x_1}/c_s^1 = c_s^{x_2}/c_s^d = \exp\left(-\frac{\mu_s^E(x_1)}{RT}\right)$ is the partition coefficient.

By using Eq. (14) we have derived the expression for σ in a very straightforward way, with the solute partition coefficient coming in very naturally. For the frictional model found in the literature one can object that it equates the total force of friction with $\operatorname{grad}\mu_i = \bar{V}_i \operatorname{grad} p + \operatorname{grad}\mu_i^c$. This is wrong because the gradient of the unaugmented chemical potential does not contain μ_i^E, i.e., potential interaction between membrane and solute, and thus it is not the total driving force. This obvious mistake is then annulled by the fact that the solute partition coefficient is introduced, though in a very artificial way (e.g., Lakshminarayanaiah 1984).

Acknowledgements. The authors thanks Prof. S. Przestalski for reading and discussing the manuscript. This work was supported by the Central Programme of Basic Research No. 02.11.

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