

DERIVATION OF PRACTICAL KEDEM - KATCHALSKY EQUATIONS FOR MEMBRANE SUBSTANCE TRANSPORT

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Abstract

The following paper includes a derivation of practical Kedem-Katchalsky (K-K) equations for the volume flow J_v and the solute flow J_s for non-electrolytes. This derivation makes the equations clearer and consequently their interpretation also becomes easier. The equations have been derived on the basis of the analysis of the membrane transport generated by simultaneous action of two thermodynamic stimuli: the hydrostatic

pressure difference Δp and the osmotic pressure difference $\Delta \Pi$. Furthermore, the derivation of the solute permeability coefficient ω , which results from K-K equations, is also presented in this paper. The formulas for coefficients characterizing membrane permeability, ω_d and ω_k , as well as their derivation and physical interpretation are also presented below. Finally, a formula for the membrane coefficient L_D , which represents a diffusional mobility, is derived.

1 Introduction

Membrane transport for binary non-electrolyte solutions, generated by the hydrostatic pressure difference Δp and the osmotic pressure difference $\Delta\Pi$, can be described by practical Kedem-Katchalsky equations. The K-K equations have been derived from the principles of linear thermodynamics of irreversible processes. Such membrane transport is described by the equations for the volume flow J_ν and the solute flow J_s [1-4]:

$$J_\nu = L_p \Delta P - L_p \sigma \Delta \Pi, \quad (1)$$

$$J_s = \omega \Delta \Pi + \bar{c}(1 - \sigma) J_\nu, \quad (2)$$

where \bar{c} stands for mean concentration, $\bar{c} \approx \frac{1}{2}(c_1 + c_2)$ and (L_p, σ, ω) are coefficients of filtration, reflection and permeation, respectively.

The above equations have widely been used in research on substance permeability through artificial and biological membranes [6, 11]. This paper includes a complete analysis and interpretation of the K-K equations. Some preliminary results in this field are presented in Ref. [15].

In the following paper the transport K-K equations have been derived on the basis of phenomenological equations. Consequently, the K-K equations have become more comprehensible and we can interpret them thoroughly. It is important from biological point of view since the effects of substance transport through biological and artificial membranes can be understood easily, whereas the application of the K-K equations in their classical version is limited to membrane systems with two-component solutions, sufficiently diluted and well stirred [7, 9,16]. The presented way of deriving these equations leads to the derivation of membrane permeability parameters ω_d , ω_k as well as L_D parameter. The physical meaning of these parameters is presented further in the paper.

2 Scheme of the solute fluxes across a membrane

Fig. 1 depicts a cell, which consist of two compartments with a solution separated by the membrane in isothermal conditions. Substance transport is generated by the simultaneous action of two stimuli: the osmotic pressure difference and the mechanical pressure difference. The solute fluxes transport through the membrane is described in the text.

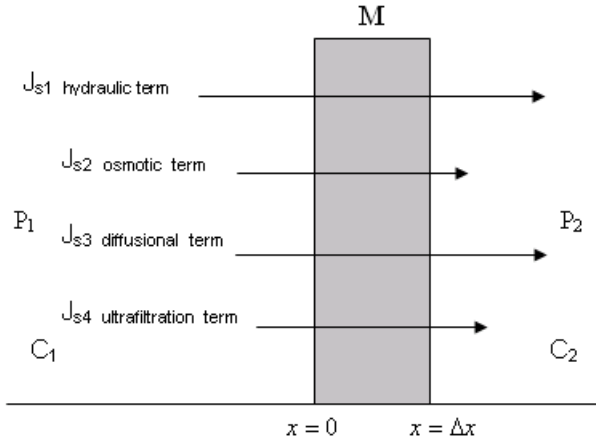


Fig. 1. A sketch of the solute fluxes transport through a membrane: M is the membrane of the thickness Δx ; C_1 and C_2 are the concentrations of solutions in compartments separated by the membrane; J_{s1} , J_{s4} are the solute fluxes caused by the hydrostatic pressure difference and J_{s2} , J_{s3} are the solute fluxes caused by the osmotic pressure difference.

The above K-K equations, (1) and (2), are derived on the basis of linear thermodynamics of irreversible processes. Membrane transport is generated by two thermodynamic stimuli: Δp and $\Delta \Pi$. In the method developed here, the analysis of the membrane transport is presented for the case of a homogeneous membrane, which separates two aqueous well-mixed solutions of a non-electrolyte with two-component solutions. There are the following conditions inside the compartments: $c_1 > c_2$ and $p_1 > p_2$. The osmotic pressure difference $\Delta \Pi$, on the basis of van't Hoff's formula, is assumed as $\Delta \Pi = RT \Delta c$ where $\Delta c = c_1 - c_2$ is the concentration difference [5, 14] while R and T are the gas constant and thermodynamic temperature, respectively. The hydrostatic pressure difference $\Delta p = p_1 - p_2$. According to the isothermal conditions, the temperature gradient equals 0.

3 Derivation of Kedem-Katchalsky equations for membrane transport from phenomenological equations

Dissipation function Φ for the membrane of thickness Δx is given by the following formula (Katchalsky and Curran, 1965):

$$\int_0^{\Delta x} \Phi dx = \Phi = \sum_{i=1}^n J_i \Delta \mu_i = J_w \Delta \mu_w + J_s \Delta \mu_s, \quad (3)$$

where J_i is the volume flow, and μ_i is the chemical potential of solution components. Equation (3) describes n different flows in terms of n forces. The subscripts w and s denote the solvent and the solute, respectively. Provided the chemical potentials at the membrane surfaces are identical to the corresponding chemical potentials in the solutions, Φ can be expressed as [2]

$$\Phi = (J_w \tilde{V}_w + J_s \tilde{V}_s) \Delta p + \left(\frac{J_s}{\tilde{c}_s} \right) \Delta \Pi, \quad (4)$$

where \tilde{V}_w and \tilde{V}_s are the partial molar volume of solvent and solute; J_w and J_s are flows of solvent and solute, respectively. We obtain the transformed dissipation function in the following form

$$\Phi = J_\nu \Delta p + J_D \Delta \Pi. \quad (5)$$

In the conditions of two thermodynamic stimuli Δp and $\Delta \Pi$, the phenomenological K-K equations for the volume flow (J_ν) and the diffusion flow (J_D) through the membrane and the forces defined by Eq. (5) can be written as

$$J_\nu = L_p \Delta p + L_{pD} \Delta \Pi, \quad (6)$$

$$J_D = L_{Dp} \Delta p + L_D \Delta \Pi, \quad (7)$$

where L_p , L_{Dp} , L_{pd} and L_D are coefficients of the membrane (filtration, ultrafiltration, osmotic and diffusional, respectively). If $\Delta p = \Delta P_i$, then $L_p = -L_{pD} = L_D$; J_D is the diffusional flow.

3.1 Equation for the volume flow J_ν

The overall volume flow J_ν is equal to the sum of the volume flux caused by Δp and the volume flux caused by $\Delta P i$. This overall volume flow J_ν can be given by Eq. (6).

Making use of the reflection coefficient σ , introduced originally by Staverman (1951), we can write [2]

$$\sigma = -\frac{L_p D}{L_p}. \quad (8)$$

As a result, equation (9), written below, has exactly the same form as Kedem-Katchalsky Eq. (1):

$$J_\nu = L_p \Delta P - L_p \sigma \Delta \Pi. \quad (9)$$

The relation among transport parameters L_p and σ is expressed in the following definition:

$$L_p = \left(\frac{J_\nu}{\Delta p} \right)_{\Delta \Pi=0}. \quad (10)$$

The parameter L_p is the hydraulic conductivity or the mechanical filtration coefficient of a given membrane. This coefficient has the character of mobility and represents the velocity of fluid per unit of pressure difference [7]. It expresses the overall filtration properties of all pores within a given membrane.

The parameter σ is the reflection coefficient. If $\sigma = 1$, the membrane is semi-permeable, what means that it is permeable only for the solvent but not for the solute molecules, which are reflected. If $\sigma = 0$, the membrane is not selective, so every pore of the membrane is permeable for the solvent as well as for the solute. If $0 < \sigma < 1$, the membrane is selective, which means that it has pores with differentiated diameters [6, 8].

3.2 Equation for the solute flow (J_s)

The overall solute flow J_s through the membrane, generated by Δp and $\Delta \Pi$, can be written in the following form [2]

$$J_s = \bar{c}(J_\nu + J_D). \quad (11)$$

For such a membrane, the Onsager reciprocal relation (ORR) is given by

$$L_{pD} = L_{Dp}. \quad (12)$$

Using Eqs. (6), (7) and (12), we can write Eq. (11) for the total solute flow as follows:

$$\begin{aligned} J_s &= \bar{c}(L_p\Delta p + L_{pD}\Delta\Pi + L_{Dp}\Delta p + L_D\Delta\Pi) \quad (13) \\ &= \bar{c}L_D\Delta\Pi + \bar{c}L_{pD}\Delta\Pi + \bar{c}(L_p + L_{Dp})\Delta p, \\ &= \bar{c}(L_D + L_{pD})\Delta\Pi + \bar{c}(L_p + L_{Dp})\Delta p, \end{aligned}$$

where $L_p\Delta p$ is the hydraulic term; $L_{pD}\Delta\Pi$ is the osmotic term; $L_{Dp}\Delta p$ is the ultrafiltration term and $L_D\Delta\Pi$ is the diffusional term.

Next, according to Eq. (8), Eq. (13) can be expressed as:

$$J_s = \omega_d\Delta\Pi + \bar{c}(1 - \sigma)L_p\Delta p. \quad (14)$$

After taking Eq. (6) into account and after some transformations, Eq.(14) can be written as:

$$\begin{aligned} J_s &= \bar{c}L_D\Delta\Pi + \bar{c}L_{pD}\Delta\Pi + \bar{c}(1 - \sigma)(J_v - L_{pD}\Delta\Pi) \quad (15) \\ &= \bar{c}L_D\Delta\Pi + \bar{c}\sigma L_{pD}\Delta\Pi + \bar{c}(1 - \sigma)J_v. \end{aligned}$$

Using Eq. (8), we can express Eq. (15) in the following form:

$$J_s = \bar{c} \left(\frac{L_D L_p - L_{pD}^2}{L_p} \right) \Delta\Pi + \bar{c}(1 - \sigma)J_v. \quad (16)$$

If in Eq. (16) we insert the coefficient [2]:

$$\omega = \left(\frac{J_s}{\Delta\Pi}_{J_v=0} \right) = \bar{c} \left(\frac{L_D L_p - L_{pD}^2}{L_p} \right), \quad (17)$$

then Eq. (16) for the solute flow J_s has the same form as Kedem-Katchalsky Eq. (2):

$$J_s = \omega\Delta\Pi + \bar{c}(1 - \sigma)J_v. \quad (18)$$

The phenomenological K-K equations can also be written in the following form [12, 13]:

$$J_v = L_p\Delta p - L_{pD}\Delta\Pi, \quad (19)$$

$$J_D = -L_{Dp}\Delta p + L_D\Delta\Pi. \quad (20)$$

3.3 Equation for the volume flow (J_ν)

Taking Eqs. (19) and (20) into account, we can rewrite the Stavermann relation, given by Eq. (8), in the following form [6, 12, 13]:

$$\sigma = \frac{L_p D}{L_p}. \quad (21)$$

According to Eq. (21), Eq. (19) for the volume flow J_ν can be expressed in the same way as Kedem-Katchalsky Eq. (1):

$$J_\nu = L_p \Delta p - L_p \sigma \Delta \Pi. \quad (22)$$

3.4 Equation for the solute flow (J_s)

According to Eqs. (12), (19) and (20), equation (11) for the total solute flow J_s can be written as follows

$$\begin{aligned} J_s &= \bar{c}(L_p \Delta p - L_{pD} \Delta \Pi - L_{Dp} \Delta p + L_D \Delta \Pi) \\ &= \bar{c}(L_p - L_{Dp}) \Delta p + \bar{c} L_D \Delta \Pi - \bar{c} L_{pD} \Delta \Pi. \end{aligned} \quad (23)$$

Using Eq. (21) and Eq. (19) we obtain:

$$\begin{aligned} J_s &= \bar{c}(1 - \sigma) L_p \Delta p + \bar{c} L_D \Delta \Pi - \bar{c} L_{pD} \Delta \Pi \\ &= \bar{c}(1 - \sigma)(J_\nu + L_{pD} \Delta \Pi) + \bar{c} L_D \Delta \Pi - \bar{c} L_{pD} \Delta \Pi \\ &= \bar{c}(L_D - \sigma L_{pD}) \Delta \Pi + \bar{c}(1 - \sigma) J_\nu \\ &= \bar{c} \left(\frac{L_D L_p - L_{pD}^2}{L_p} \right) \Delta \Pi + \bar{c}(1 - \sigma) J_\nu. \end{aligned} \quad (24)$$

If in Eq. (24) we insert Eq. (17) for the coefficient ω , then the equation Eq. (24) for the solute flow J_s has the same form as Eq. (2):

$$J_s = \omega \Delta \Pi + \bar{c}(1 - \sigma) J_\nu, \quad (25)$$

where ω is the coefficient of a solute permeability at $J_\nu = 0$. It expresses the permeation of all pores of a given membrane with simultaneous action of both stimuli, $\Delta \Pi$ and Δp .

4 Derivation of membrane transport parameters:

ω_d , ω_k and L_D

4.1 Membrane permeation coefficient ω_d

Parameter ω_d is a coefficient expressing permeation of all pores of a given membrane for the solute flow due to the presence of $\Delta\Pi$ stimulus, when $\Delta p = 0$. For the sake of its derivation, we define the coefficient ω_d in the following way

$$\omega_d = \left(\frac{J_s}{\Delta\Pi} \right)_{\Delta p=0}. \quad (26)$$

Using Eqs. (9) and (18), we obtain the following relation:

$$\begin{aligned} J_s &= \omega\Delta\Pi + \bar{c}(1-\sigma)(L_p\Delta p - L_p\sigma\Delta\Pi) \\ &= [\omega - \bar{c}(1-\sigma)L_p\sigma]\Delta\Pi + \bar{c}(1-\sigma)L_p\Delta p. \end{aligned} \quad (27)$$

When $\Delta p = 0$, Eq. (27) takes on the form:

$$(J_s)_{\Delta p=0} = (\omega - \bar{c}(1-\sigma)L_p\sigma)\Delta\Pi. \quad (28)$$

The obtained equation, Eq. (28), allows one to calculate the ω_d coefficient due to its definition given by Eq. (26). Therefore, ω_d can be expressed as:

$$\omega_d = \omega - (1-\sigma)\bar{c}L_p\sigma. \quad (29)$$

Next, inserting Eq. (17) and Eq. (8) into Eq. (30), we get the final form of the ω_d coefficient [11]:

$$\begin{aligned} \omega_d &= \bar{c}(L_D + \sigma L_{pD} - L_p\sigma + \sigma L_p\sigma) \\ &= \bar{c}(L_D + L_{pD}). \end{aligned} \quad (30)$$

The coefficient ω_d , expressed by Eq. (30), can be interpreted more easily than the one expressed by Eq. (29). Moreover, the form of Eq. (30) makes membrane transport, described by practical Kedem-Katchalsky equations, more comprehensible.

4.2 Parameter L_D :

The above equations (30) and (29) can be written as follows:

$$\bar{c}(L_D + L_p D) = \omega - (1 - \sigma)\bar{c}L_p\sigma. \quad (31)$$

The final formula describing transport parameter L_D has the following form [11]:

$$L_D = \frac{\omega}{\bar{c}} + L_p\sigma^2. \quad (32)$$

The diffusional flow J_D , caused by the osmotic pressure difference, is characterized by the coefficient L_D . This coefficient represents diffusional mobility per unit of osmotic pressure [2]. Therefore, the coefficient L_D can be defined as:

$$L_D = \left(\frac{J_D}{\Delta\Pi} \right)_{\Delta p=0}. \quad (33)$$

4.3 Transport parameter ω_k

Parameter ω_k is a permeation coefficient of all pores of a given membrane for the solute flow due to the action of the hydrostatic pressure difference Δp , when $\Delta\Pi = 0$. The coefficient ω_k can be defined by means of the following formula

$$\omega_k = \left(\frac{J_s}{\Delta p} \right)_{\Delta\Pi=0}. \quad (34)$$

After taking Eqs. (18) and (9) into account, we obtain Eq. (33) in the following form

$$\omega_k = \bar{c}(1 - \sigma)L_p. \quad (35)$$

Inserting Eq. (8) into Eq. (34), we can write eventually the formula for the coefficient ω_k as:

$$\omega_k = \bar{c}(L_p + L_{Dp}). \quad (36)$$

5 Conclusions

The analysis of the expressions for particular fluxes and other relations derived here, representing membrane permeation coefficients ω_d , ω_k , ω and parameter L_D , together with their physical interpretation, make practical K-K equations more straightforward and comprehensible. Hence, the physical interpretation of these equations seems to be easier now, while it has been considered as difficult especially in the case of the equation for the solute flow J_s .

The method presented here, which has resulted in the derivation of practical Kedem-Katchalsky equations for the volume flow J_v and the solute flow J_s , allows one to carry out a more detailed and comprehensible analysis of results of the research on transport through biological and artificial membranes.

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Kedem-Katchalsky equations for membrane substance transport

Nomenclature

$J_s, J_{s1}, J_{s2}, J_{s3}, J_{s4}$	solute fluxes
J_v	volume flow
ν_s, ν_w	velocity of solute and solvent
μ_i	chemical potential of the i -th component
$\Delta\mu_i$	difference of the chemical potentials of the i -th component
\tilde{V}_w, \tilde{V}_s	partial molar volume of the solvent and the solute
$\Delta p, \Delta\Pi$	hydrostatic and osmotic pressure differences (Pa)
L_p, L_D, L_{pD}, L_{Dp}	hydraulic coefficients
$\omega, \omega_k, \omega_d$	solute permeability coefficients
σ	reflection coefficient (-)
\bar{c}	mean concentration
c_1, c_2	solutions concentrations
Δc	concentration difference
R	gas constant
T	absolute temperature

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It is a good way to clarify some chapters of the non-equilibrium thermodynamics.

This derivation, in particular makes the equation for solute flow (J_s) and the solute permeability coefficient (ω) clearer and consequently their interpretation also becomes easier. Furthermore, this paper makes some new contribution to membrane expressed by the so called K-K equations. It includes a transformation of K-K equation on solute flow to its new form: $J_s = \omega_d \Delta \Pi + \bar{c}(1 - \sigma)L_p \Delta p$ as coefficient derivations which characterize the membrane (ω_d - the coefficient of diffusive solute permeation and L_D - conductivity for

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It should be emphasized that the K-K equation on solute flow transformed to a new form is more comprehensible. Together with the derivated parameters, it gives new opportunities for the research concerning solute permeation across biological and artificial membranes.

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