

A Practical Method for the Analysis of Osmotic-and-Diffusive Energy Conversion

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Abstract. A practical method for the study of osmotic- and-diffusive conversion of free energy of solutions with different concentrations is presented. Equations for effective power, dissipative power, total power and energetic efficiency have been derived for fixed membrane systems. These equations allow energetic evaluation of these systems. The significance of the method for biological studies is also suggested.

Key words: Osmosis — Diffusion — Energy — Power — Energetic efficiency

Introduction

Osmosis, as the process of passive permeation of solvent across a selective or semipermeable membrane, is one principal way how to convert free energies of differently concentrated solutions to effective energy (work against external forces). The principle is based on the fact that osmotic fluxes can be directed against external forces. This allows membrane systems to perform useful work.

When selective membranes are used in similar systems, osmosis is always accompanied by solute diffusion. Diffusion can also be considered as a free energy conversion device. In this case however, only energy dissipation occurs in the system, since diffusion is a dissipative process.

The energetic aspects of osmosis and diffusion have been studied from biophysical (Kedem and Caplan 1965; Peusner 1983, 1985; Kargol 1985) as well as technological (Lee et al. 1981; Loeb 1976; Levenspiel 1974) points of view. Biophysical studies have been concentrated on the energetic efficiency of osmotic water transport within and between cells. Water pumping in plants (against the gravity force, by xylem elements) caused by osmotically generated root pressure (Anderson 1976; Ginsburg 1971; Pitman 1982; Kargol 1978; Katou et al. 1987; Przystalski and Kargol 1987), or water transport in plant xylem due — according to the graviosmotic hypothesis (Kargol 1978; Przystalski and

Kargol 1987) — to graviosmosis, have also been considered by Kedem and Caplan (1965) and Peusner (1983, 1985). These authors performed a detailed analysis of energetic efficiency of osmotic systems. They used the efficiency definition:

$$\eta = - \frac{J_1 X_1}{J_2 X_2}$$

where J_1, J_2 are fluxes and X_1, X_2 are forces associated with these fluxes.

The present paper will choose a different approach to the problem of osmotic-and-diffusive energy conversion. Using the Kedem-Katchalsky practical equation we developed (for suitable membrane systems) proper explicit expressions for effective power, dissipative power, total power and efficiency. Under the known efficiency we understand the effective to total power ratio. The expressions obtained allow energetic evaluation of membrane systems in which similar energy conversion occurs. Where appropriate, the membrane systems were considered to be analogical to respective electrical networks. In general, we tried to develop a relatively easily understandable, more complex and therefore competitive, method of solving energetic problems of osmotic-and-diffusive energy conversion. Some preliminary information concerning this method was presented previously (Kargol 1985). The present paper gives a complete description of the method. The method has recently been partly experimentally verified by us.

Analytic description of the osmotic-and-diffusive conversion of energy

1. Membrane system and transport equations

A two-membrane system as shown in Fig. 1a will be considered. In this system, membrane M with surface S , filtration coefficient L_p , reflection coefficient σ and permeability ω separates two compartments, A and B, each filled with a well-mixed solution differing in concentration ($C_1 < C_2$). As a result, osmotic volume flow J_v is generated on the membrane. Membrane M¹ with filtration coefficient L , permeability ω_1 and reflexion coefficient $\sigma_1 = 0$ separates compartments B and C both filled with solutions with concentration C_2 . This membrane will be considered as energy acceptor. Let us assume, for the sake of simplification, that mechanical pressures in the outer compartments are identical ($P_A = P_C = P_0$). We will also assume that the volumes of all the three compartments are sufficiently large so that permeation processes can be regarded as quasi-stationary (with fixed active surfaces S of the membranes). The membrane system can be represented by electrical scheme shown in Fig. 1b. The electric current source with electromotive force E corresponds to membrane M, in which effective difference $\sigma\Delta\pi$ of osmotic pressure occurs, and resistance R corresponds to

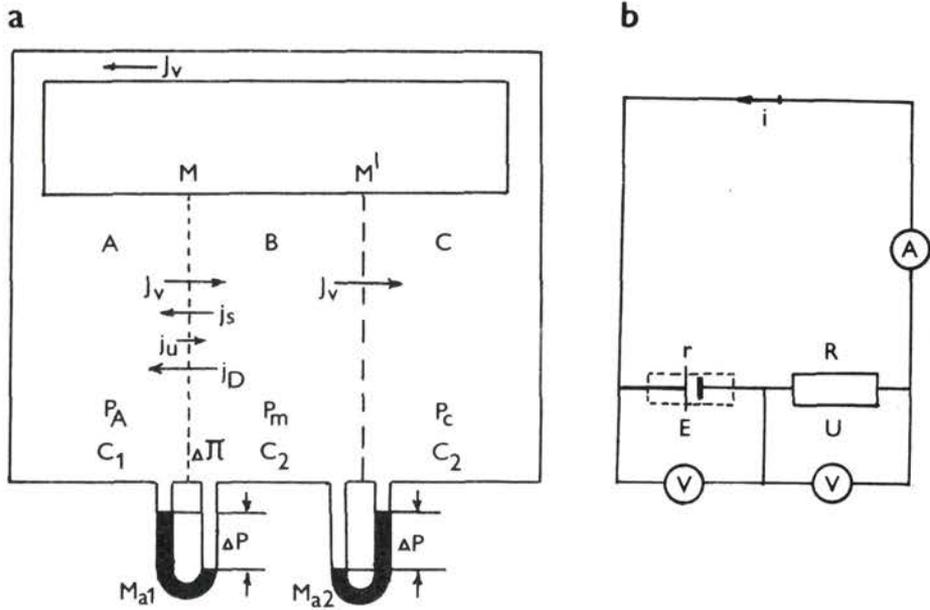


Fig. 1. Schematic representation of the osmotic system (a) and its electrical circuit analogy (b). (A, B, C — compartments, M, M' — membranes, C_1 , C_2 — concentrations of solutions, M_{a1} , M_{a2} — manometers, $\Delta\pi$ — osmotic pressure difference, ΔP — mechanic pressure difference, J_v — volume flow, r , R — electric resistance, E — electromotive force, U — voltage, i — electric current).

membrane M^1 with hydraulic resistance $R_1 = \frac{1}{L}$. Flow J_v corresponds to current intensity i . According to the Kedem-Katchalsky formalism (Katchalsky and Curran 1965) we can write, for the considered membrane system:

$$J_v = L_p \sigma \Delta\pi - L_p \Delta P, \quad (1)$$

where: $\Delta P = P_m - P_o$, and P_m is the osmotically generated mechanical pressure in compartment B. In agreement with the principles of hydrodynamics, a pressure decrease ΔP will occur across both membranes and will be indicated by manometers M_{a1} and M_{a2} (Fig. 1a). Pressure difference ΔP across membrane M^1 will be considered as external pressure. Flux J_v flows across membrane M^1 . Therefore we can write:

$$J_v = L \Delta P. \quad (2)$$

Using Eqs. (1) and (2) we get:

$$J_v = \frac{LL_p \sigma \Delta \pi}{L + L_p} \quad (3)$$

Introducing $\frac{1}{L} = R_1$ and $\frac{1}{L_p} = r_1$, equation (3) can be rewritten in the form analogical to the Ohm law:

$$J_v = \frac{\sigma \Delta \pi}{R_1 + r_1}, \quad \left(i = \frac{E}{R + r} \right)$$

With a selective membrane (i.e. $0 < \sigma < 1$) the solute flux j_s across the membrane will also occur. This flux can be described by:

$$j_s = \omega \Delta \pi - (1 - \sigma) \bar{c} J_v \quad (4)$$

where: \bar{c} is the average concentration $\left(\bar{c} = \frac{C_1 - C_2}{\ln \frac{C_1}{C_2}} \right)$.

The particular terms in equation (4):

$$j_D = \omega \Delta \pi \quad (5)$$

$$j_u = (1 - \sigma) \bar{c} J_v \quad (6)$$

represent the diffusion flux (j_D) and the solvent flux (j_u) carried by osmotic flow J_v in membrane stomata.

2. Power equations and expression for the energetic efficiency of osmosis

For the considered membrane system the following conditions are valid:

- If membrane M is semipermeable ($\sigma = 1$), then free energy conversion can occur only on the osmotic principle.
- If membrane M is selective ($0 < \sigma < 1$), then, due to the existence of fluxes J_v and j_s , both osmotic and diffusive energy conversion are possible.
- If membrane M is permeable ($\sigma = 0$), then only diffusive conversion (dissipation) of energy will occur.

We will be concerned with the most general case, the osmotic-and-diffusive conversion of free energy. We will consider free energy conversion to effective work, free energy dissipation and conversion efficiency. Eqs. (1) and (4) will be used for the analysis of the osmotic and diffusive conversion respectively.

Osmotic conversion. Let us multiply equation (1) by factor $S \frac{J_v}{L_p}$ and rewrite it

in the form

$$S\sigma\Delta\pi J_v = S \frac{J_v^2}{L_p} + S\Delta P J_v \quad (7)$$

where S is the membrane surface.

We will term the equation obtained the global power equation. In accordance with $M = Fv = S\Delta P v$, the particular terms

$$M'_{co} = S\sigma\Delta\pi J_v \quad (8)$$

$$M_{ro} = S \frac{J_v^2}{L_p} \quad (9)$$

$$M_{uo} = S\Delta P J_v \quad (10)$$

denote sum of powers (M'_{co}); power (M_{ro}) dissipated in membrane M , i.e. the amount of energy dissipated in a unit of time because of solution viscosity; and effective power (M_{uo}) absorbed and emitted by membrane M^1 considered as energy acceptor. According to Eq. (7),

$$M'_{co} = M_{ro} + M_{uo}.$$

It should be noted that similar considerations concerning an electrical circuit (see Fig. 1b) yield

$$Ei = ri^2 + Ui$$

where $Ei = M'_c$ is the sum of powers, $ri^2 = M_r$ is the power dissipated on resistance r , $Ui = M_u$ is the power emitted on resistance R , in analogy to Eq. (7). Flux j_u against concentration gradient is associated with volume flow J_v according to equation (4). This means that the membrane system derives, during the process of osmosis, a certain power M_{uD} as a result of the existence of this flux. Hence, the principle of energy conversion can be written as

$$M_{co} = M_{ro} + M_{uo} + M_{uD}, \quad (11)$$

Where M_{co} is the total power.

Introducing (2), equation (7) can be rewritten as

$$S\sigma\Delta\pi J_v = S \frac{J_v^2}{L_p} + S \frac{J_v^2}{L}. \quad (12)$$

This equation implies that the smaller the value of parameter L (relative to parameter L_p), the greater the power M_{uo} emitted in membrane M^1 . On the other hand, a decrease of this parameter is associated with a decrease of flux J_v , which

in turn results in a decrease of power M_{uo} , according to

$$M_{uo} = S \frac{J_v^2}{L}, \quad (13)$$

In this case, it is interesting to analyze this power as a function of L . For this purpose let us consider Eq. (13) which after introducing (3) has the form

$$M_{uo} = S \frac{LL_p^2 \sigma^2 \Delta\pi^2}{(L + L_p)^2}. \quad (14)$$

The analogic expression for electrical circuit is

$$M_u = \frac{RE^2}{(R + r)^2}.$$

Equation (14) allows a detailed analysis of effective power M_{uo} as function of S , L , L_p , σ and $\Delta\pi$. It can be concluded, among other, that:

- $M_{uo}(L) \rightarrow 0$ if $L \rightarrow 0$ or $L \rightarrow \infty$,
- $M_{uo}(L) > 0$ for $0 < L < \infty$,
- Function $M_{uo}(L)$ possesses a maximum for $L = L_p$,
- The value of function $M_{uo}(L)$ at the maximum point $L = L_p$ is

$$M_{uo}^{\max} = \frac{1}{4} SL_p \sigma^2 \Delta\pi^2. \quad (15)$$

Lee et al. (1981) have come to the same equation.

The problem of dissipated power can be analyzed in a similar way. Let us now calculate the energetic efficiency η_o of osmosis in the system considered. The efficiency here means the ratio of effective power M_u to total power M_c :

$$\eta_o = \frac{M_u}{M_c}. \quad (16)$$

Using this definition and equation (1), (8) and (10) we obtain

$$\eta_o = \frac{M_{uo}}{M'_{co}} = \frac{\Delta P}{\sigma \Delta\pi} = 1 - \frac{J_v}{L_p \sigma \Delta\pi} = 1 - \frac{L}{L + L_p}. \quad (17)$$

where $M'_{co} = M_{co} - M_{uD}$.

This equation enables us to evaluate efficiency η_o as a function of L and L_p . It should be noted that the expression

$$\eta = 1 - \frac{ri}{E}$$

is the electrical analogy of Eq. (17).

Let us now consider the diffusive conversion of energy.

First of all it should be noted that, because $0 < \sigma < 1$, fluxes J_v and j_s will flow across membrane M simultaneously. This means that both the osmotic and the diffusive conversion of energy will occur in the system. In general, power M_D dissipated during the process of diffusion can be expressed as

$$M_D = \frac{\Delta G}{\Delta t} = \frac{\Delta n}{\Delta t} (u_2 - u_1)$$

where ΔG is the change in free energy of the system at time Δt ; Δn is the number of moles of the solute; which has diffused across membrane M ; $(u_2 - u_1)$ is the difference in the chemical potentials. To solve the problem of diffusive energy conversion fluxes j_s , j_D and j_u are related to volume units:

$$j_{vs} = \frac{j_s}{\bar{c}} = \frac{\omega}{\bar{c}} \Delta\pi - (1 - \sigma) J_v \quad (18)$$

$$j_{vD} = \frac{\omega}{\bar{c}} \Delta\pi \quad (19)$$

$$j_{vu} = (1 - \sigma) J_v \quad (20)$$

Multiplying Eq. (18) by $S\Delta\pi$ the following power equation is obtained:

$$Sj_{vs}\Delta\pi = S \frac{\omega}{\bar{c}} \Delta\pi^2 - S(1 - \sigma) J_v \Delta\pi \quad (21)$$

In this equation, according to the basic formula of mechanics $M = Fv$, the particular terms

$$M_{rD} = S \frac{\omega}{\bar{c}} \Delta\pi^2 \quad (22)$$

$$M_{uD} = S(1 - \sigma) J_v \Delta\pi \quad (23)$$

$$M_{sD} = Sj_{vs}\Delta\pi \quad (24)$$

express: M_{rD} the power dissipated due to the presence of flux j_D ; M_{uD} the power recovered in terms of free energy as a result of removing solute molecules by flow J_v (in stomata of membrane M). M_{sD} is the difference between M_{rD} and M_{uD} . According to Eq. (21),

$$M_{sD} = M_{rD} - M_{uD} \quad (25)$$

3. The total energetic efficiency of the system

According to our previous considerations and using the energy conservation law we can write (see (11) and (25)):

$$M_{co} + M_{sD} = M_{uo} + M_{ro} + M_{rD} = M_c. \quad (26)$$

Next, applying the general definition of efficiency (16) and Eqs. (1), (2), (9), (13), (22), (26) we obtain the expression for total energetic efficiency of the osmotic-and-diffusive conversion of energy:

$$\begin{aligned} \eta_{oD} &= \frac{M_{uo}}{M_{uo} + M_{ro} + M_{rD}} = \frac{\frac{J_v^2}{L}}{\frac{J_v^2}{L} + \frac{J_v^2}{L_p} + \frac{\omega}{\bar{c}} \Delta\pi^2} = \\ &= \frac{L_p \Delta P (\sigma \Delta\pi - \Delta P)}{L_p \sigma \Delta\pi (\sigma \Delta\pi - \Delta P) + \frac{\omega}{\bar{c}} \Delta\pi^2} \end{aligned} \quad (27)$$

Introducing Eq. (3) to this expression we get:

$$\eta_{oD} = \frac{LL_p^2 \sigma^2}{LL_p^2 \sigma^2 + L^2 L_p \sigma^2 + \frac{\omega}{\bar{c}} L^2 + 2 \frac{\omega}{\bar{c}} LL_p + \frac{\omega}{\bar{c}} L_p^2} \quad (28)$$

The following, intuitively obvious, conclusions can be drawn based on this equation:

a) For $L_p = 0$, $\eta_{oD} = 0$

b) If $L_p = \infty$, then $\eta_{oD} = \frac{L\sigma^2}{L\sigma^2 + \frac{\omega}{\bar{c}}}$. Moreover, assuming $\sigma = 1$ (which implies

$\omega = 0$), $\eta_{oD} = 1$.

c) $\eta_{oD} = 0$ if $L = 0$ or $L = \infty$, for fixed L_p .

d) Function $\eta_{oD}(L)$ has a maximum for $L = L_p$.

e) The value of the function at the maximum point $L = L_p$ is

$$\eta_{oD}^{\max} = \frac{L\sigma^2}{2L\sigma^2 + 4 \frac{\omega}{\bar{c}}}$$

Moreover, assuming $\sigma = 1$, $\eta_{oD}^{\max} = \frac{1}{2}$.

It should be also emphasized that if $L = \infty$ (this means in practice that membrane M^1 is absent), then equation (12) is reduced to

$$S\sigma\Delta\pi J_v = S \frac{J_v^2}{L_p}$$

It is obvious from this equation that the whole osmotically emitted power is dissipated in membrane M .

Conclusions

This work deals with osmosis and diffusion as the ways of conversion of free energy of solutions with different concentrations. A two-membrane osmotic system has been considered. This system can be represented by an electrical circuit consisting of external resistance R and a cell with electromotive force E and internal resistance r . Equations have been derived for dissipative power, effective power, total power as well as for energetic efficiency. As mentioned in Introduction, these equations allow to analyze in detail the osmotic-and-diffusive conversion of free energy in membrane systems. Nevertheless, they require experimental confirmation. Results of partial verification will be presented elsewhere.

To conclude, it should be noted that the problems of the osmotic-and-diffusive energy conversion become a little more complicated if membrane M^1 is selective or semipermeable. These cases will be analyzed in our further studies. This work was performed within the Research Problem CPBP 05.02.

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