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On the Volume Flow in Nonequilibrium Membrane Systems

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Synopsis. The volume flow definitions of the different formulations which describe irreversible proccesses in isothermal membrane systems are critically analysed. We show that only one of these definitions can be considered as the volume change observed in each compartment. The study carried out considers the general case of multicomponent systems with arbitrary dissociation degrees.

Nonequilibrium thermodynamics studies irreversible processes from the dissipation function, which can be written as a sum of the products of generalized forces and the corresponding generalized flows.

In the case of a nonequilibrium isothermal membrane system the dissipation function is

$$\Psi=\sum_{i=1}^{m} J_i^* \,\Delta\tilde{\mu}_i, \tag{1}$$

where J_i^* denotes the matter flow of species i from subsystem″ to subsystem′, and $\Delta\tilde{\mu}_i=\tilde{\mu}_i''-\tilde{\mu}_i'$ is the difference in the electrochemical potential. The subindex i denotes every ionic (i=1,2,...k) or neutral species (i=k+1,...m), which can move independently.

The different ways in which the dissipation function of a same nonequilibrium system can be written determine each one of the formulations which describe the irreversible processes. Some formulations of nonequilibrium isothermal membrane systems make use of the volume flow.[1–8] Commonly this flow is considered as the volume change observed in each compartment. In this paper we would like to point out several questions concerning the definitions of this flow in the most important formulations, solving the difficulties showed by Weinstein[9] and Kedem.[10]

Some formulations are developed only for binary solutions with a completely dissociated electrolyte. Our aim here is to study these systems in a more general way. Thus, multielectrolyte solutions, with arbitrary values of dissociation degrees, will be considered.

The dissipation function expressed in terms of directly observed variables is:[11]

$$\Psi=q\Delta P+\sum_{k+1}^{m-1} J_i^m \,\Delta\mu_i^c+I\Delta\psi, \tag{2}$$

where q is the apparent volume rate in subsystem′; ΔP=P″−P′ stands for the difference in pressure; J_i^m are the electrolyte flows relative to the solvent (denoted by m); $\Delta\mu_i^c$ is the difference in the concentration-dependent part of the chemical potential of the neutral species (i=k+1,...m−1); I denotes the charge flow and $\Delta\psi$ the difference in electrical potential between the electrodes, which are reversible to inonic species 1.

The volume flow in this formulation has the following characteristics:

a) In terms of the matter flows through the membrane, J_i^*, q must be expressed as

$$q=\sum_{i=1}^{m} J_i^* \,\bar{V}_i-J_1^e\bar{V}_1+\frac{I}{z_1F}v_x, \tag{3}$$

where J_1^e is the flow of the ionic species 1 from subsystem′ to the electrode; $\bar{V}_i$ is the value of the partial molar volume of species i; v_x is the molar volume of the chemical species in the electrode. We can easily see that J_1^e is related to I through

$$I=z_1F\,J_1^e. \tag{4}$$

The first two terms of the right-hand member in Eq. 3 are the real volume rate of subsystem′ and the third term represents the electrode volume rate. This is the reason why q is the apparent volume rate in subsystem′.

b) The volume flow q is meausured by the movement of the solution-air meniscus in a capillary attached to subsystem′. Then, q is a directly observed variable.

c) q can be written in terms of the electrolyte flows which arrive to subsystem′, J_i (i=k+1, ...m). These flows have two contributions: 1) The matter flows through the membrane J_i^*. 2) The contribution of the flow J_1^e from the subsystem′ to the electrode. In terms of these variables the volume flow has the expression:

$$q=\sum_{i=k+1}^{m} J_i \,\bar{V}_i+\frac{I}{z_1F}v_x. \tag{5}$$

This result is valid regardless of the dissociation degree values of the electrolytes.[11]

The variables involved in the dissipation function of Eq. 2 determine one of the thermodynamic formulations of the irreversible processes which occur in isothermal membrane systems. Other formulations making use of volume flows are possible, as we can see in the following.

The expression for the volume flow in the Mazur-Overbeek's formulation[12] is

$$q^*=\sum_{i=1}^{m} J_i^* \,\bar{V}_i, \tag{6}$$

then the dissipation function can be written as

$$\Psi=q^*\,\Delta P+\sum_{k+1}^{m-1} J_i^m \,\Delta\mu_i^c+I\,\Delta\psi^*, \tag{7}$$

where

$$\Delta\psi^*=\Delta\psi+\frac{v_x-\bar{V}_1}{z_1F}\Delta P. \tag{8}$$

When $\Delta P=0$, then $\Delta\psi^*=\Delta\psi$. $\Delta\psi^*$ is related to the difference in electrical potential between the subsystems, $\Delta\psi^I$, through[13)]

$$\Delta\psi^* = \Delta\psi^I + \frac{\Delta\mu_1^c}{z_1 F}. \tag{9}$$

At the electrokinetic processes where $\Delta\mu_1^c=0$, then $\Delta\psi^*=\Delta\psi^I$.

The Kedem-Katchalsky's formulation[14,15)] assumes the liquid which flows through the membrane having only two components: a solute s and a solvent w. The solute is an electrolyte completely dissociated into two ionic species according to the coefficients ν_1 and ν_2. The solvent w is not dissociated. They define the volume flow as

$$q^0 = J_w{}^* \, \overline{V}_w + \frac{J_2{}^*}{\nu_2} \overline{V}_s, \tag{10}$$

which can also be written, taking into account the flows J_w and J_s which reach subsystem′, as

$$q^0 = J_s\overline{V}_s + J_w\overline{V}_w. \tag{11}$$

The Kedem-Katchalsky's volume flow can be expressed in a more general way. For multicomponent systems with arbitrary values of dissociation degrees, we have

$$q^0 = \sum_{i=1}^{m} J_i{}^* \, \overline{V}_i - J_1^e \, \overline{V}_1, \tag{12}$$

or also

$$q^0 = \sum_{i=k+1}^{m} J_i \, \overline{V}_i. \tag{13}$$

As we can see, q^0 is the real volume rate in subsystem′. Making use of flow q^0, the dissipation function takes the form

$$\Psi = q^0 \, \Delta P + \sum_{k+1}^{m-1} J_i^m \, \Delta\mu_i^c + I\Delta\psi^0, \tag{14}$$

where

$$\Delta\psi^0 = \Delta\psi + \frac{v_x}{z_1 F} \Delta P. \tag{15}$$

The relationships between the three volume flows are:

$$q = q^* + \frac{I}{z_1 F}(v_x - \overline{V}_1), \tag{16}$$

$$q = q^0 + \frac{I}{z_1 F} v_x. \tag{17}$$

The flow q^0 can be evaluated from direct meausurements of q by using Eq. 17. However, the flow q^* cannot be determined, except for the zero electric current case ($I=0$), because it is imposible to know the partial molar volume $\overline{V}_1$ of the ionic species 1.

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