

The Coefficients for Isothermal Transport. I. Cation Exchange Membrane and Electrodes Reversible to a Common Anion

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Isothermal transport processes across a membrane, placed between anion reversible electrodes, is described by a set of relations between fluxes and forces. The fluxes are transfer of neutral components and current. The forces are gradients in chemical potential for the neutral components, and a gradient in electric potential that can be measured between defined electrodes. Thus the presentation deals only with measurable quantities. The number and kind of components used to describe the system, conform with the phase rule. The forces used in the flux equations are therefore independent.

Restrictions of the system, such as the selectivity of the electrodes and of the membrane, and the charge of the ions composing the salts, lead to relations between the transport coefficients in addition to the Onsager reciprocal relations.

Methods for experimental determination of the transport coefficients are discussed.

1. INTRODUCTION

Irreversible thermodynamics is used for describing transport processes in membranes in various contexts.^{1–10} When treating electrolyte solutions, commonly single ion components are used. The basic fluxes and forces are ionic fluxes and gradients in electrochemical potential of ions, and the electric current is expressed as the sum over all charges carried by the ionic fluxes.^{3–5} General thermodynamic objections can be raised to the definitions of single ion quantities, and thus to their use.

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An alternative treatment considering only measurable quantities, presented previously,¹ is used in a wider context in this paper. The components of the system are the components in terms of the phase rule, and the electric current is treated as one of the basic fluxes of the system. In this way a more exact and general description of the transport processes is obtained. The physical interpretations of the coupling phenomena on this basis are limited to the macroscopic phenomenological level.

The importance of the analysis is seen when the description of the transport processes is developed for a cation exchange membrane placed between anion reversible electrodes. New information about the phenomenological coefficients is then obtained. Finally experimental conditions consistent with the theoretical treatment are outlined.

2. TRANSPORTS IN AN ION EXCHANGE MEMBRANE PLACED BETWEEN ELECTRODES REVERSIBLE TO A COMMON ANION

The system considered consists of two solutions separated by a cation exchange membrane and an anion reversible electrode in each solution. Each solution contains two electrolytes with a common anion. In our example the electrolytes are HCl and NaCl, and Ag/AgCl electrodes are used. The system is illustrated in Fig. 1.

The system is assumed to be isothermal. Any enthalpy change by the transport across

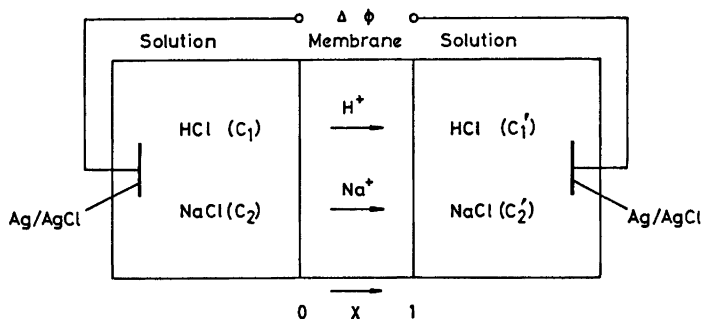


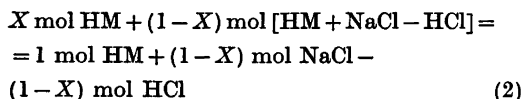
Fig. 1. A cation exchange membrane separating two solutions of HCl and NaCl. The electrodes are reversible to the Cl^- ion.

the electrolyte–membrane phase boundary is assumed to have no significant effect on the mass fluxes, *i.e.* temperature gradients are negligibly small.

In terms of the phase rule, the system contains the four components HCl, NaCl, H_2O and HM, where HM denotes the membrane in the hydrogen form. For the case of diffusive flows Hanley⁶ discussed why the membrane must be included among the components. The membrane in the sodium form, NaM, is not a component in terms of the phase rule. Assuming local equilibrium inside the membrane, NaM can be expressed by the other components in the equilibrium equation:



Thus it is always possible to avoid the component NaM, when describing a membrane consisting of X mol of HM and $(1-X)$ mol of NaM. The membrane may be considered to contain:



Mass fluxes to be considered need therefore only be J_{HCl} , J_{NaCl} , $J_{\text{H}_2\text{O}}$ and J_{HM} . According to Prigogine⁷ any reference velocity can be used to define isothermal diffusion at mechanical equilibrium. Our system is assumed to undergo only negligible changes in macroscopic kinetic energy. This means that the flux of HM, J_{HM} , can be chosen equal to zero and the other fluxes can be given relative to J_{HM} .

One may note that the amount of HM on the right hand side of eqn. (2) is always 1 mol (1 equiv.). This means that the reference, HM, is constant for all membrane compositions. The reference is also equivalent to the membrane matrix as a reference for both stationary and non-stationary flow. The membrane matrix was chosen as the reference in the “black box” description of membrane transport processes.^{3,4}

The set of flux equations. When diffusion takes place across a membrane while a current passes through the system, the changes taking place are described by fluxes of the neutral components, J_{HCl} , J_{NaCl} , $J_{\text{H}_2\text{O}}$ and the electric current, I . The second postulate of irreversible thermodynamics gives the following relations between fluxes and forces for an isothermal system:

$$J_{\text{HCl}} = J_1 = -L_{11}\nabla\mu_1 - L_{12}\nabla\mu_2 - L_{13}\nabla\mu_3 - L_{14}\nabla\phi \quad (3)$$

$$J_{\text{NaCl}} = J_2 = -L_{21}\nabla\mu_1 - L_{22}\nabla\mu_2 - L_{23}\nabla\mu_3 - L_{24}\nabla\phi \quad (4)$$

$$J_{\text{H}_2\text{O}} = J_3 = -L_{31}\nabla\mu_1 - L_{32}\nabla\mu_2 - L_{33}\nabla\mu_3 - L_{34}\nabla\phi \quad (5)$$

$$I = J_4 = -L_{41}\nabla\mu_1 - L_{42}\nabla\mu_2 - L_{43}\nabla\mu_3 - L_{44}\nabla\phi \quad (6)$$

where L_{ij} are called phenomenological coefficients.

The fluxes in the above equations are obtained by measuring the electric current and composition changes in the solutions over time. The forces can be obtained by measuring dif-

ferences in chemical or electric potential over very small differences in the space coordinates. Chemical potentials are measured by standard methods. The electric potential is measured by inserting minute electrodes reversible to the chloride ion. (If the chloride content of the membrane is equal to zero, a minute quantity of electrolyte should be in contact with each electrode). These electrodes carry no current and are not assumed to disturb the transport processes significantly, as any change in membrane properties will be only over a very limited region.

One cannot insert electrodes without introducing additional components in the system. When electrodes reversible to the chloride ion are Ag/AgCl electrodes, the additional components are Ag and AgCl. The transfer of these components is connected to the transfer of charge in a simple way:

$$J_{\text{Ag}} = I \text{ and } J_{\text{AgCl}} = -I$$

Correspondingly there is a transfer of volume from left to right equal to $I(V_{\text{Ag}} - V_{\text{AgCl}})$, where V_{Ag} and V_{AgCl} are the molar volumes of Ag(s) and AgCl(s), respectively.

The components Ag and AgCl are separate phases, they are not present in any of the other phases. This means that the gradients in their chemical potential are equal to zero unless there is a pressure gradient in the system. With a pressure gradient, ∇P , the gradients in chemical potential for the two components are:

$$\nabla \mu_{\text{Ag(s)}} = V_{\text{Ag}} \nabla P \text{ and } \nabla \mu_{\text{AgCl(s)}} = V_{\text{AgCl}} \nabla P$$

The contribution to the gradient in electric potential from these components is equal to:

$$(V_{\text{AgCl}} - V_{\text{Ag}}) \nabla P \text{ [cf. eqn. (26)]}$$

By subtracting this term from the measured electric potential gradient, $\nabla \phi_{\text{obs}}$, one obtains the gradient $\nabla \phi$ in eqns. (3-6):

$$\nabla \phi = \nabla \phi_{\text{obs}} - (V_{\text{AgCl}} - V_{\text{Ag}}) \nabla P$$

In this way one avoids operating with additional components in the basic set of equations.

The eqns. (3-6) describe the transport processes in the system on a macroscopic phenomenological level, they are not based on any model assumption. This description is as close to physical reality as can be obtained by a rigorous

thermodynamic method. A description in terms of volume flows^{3,4,8} is also independent of model assumptions, but is less precise than the present approach.

The gradients in chemical and electric potential in the system are assumed to be only across the membrane, *i.e.* no diffusive film will be considered. Any pressure gradient in the membrane is included in the gradients in chemical potential.

The gradients in chemical potential are linearly dependent through the Gibbs-Duhem equation. When energy contributions due to changes in dipole orientation are negligible, the equation does not contain gradients in electric potential. For an isothermal system where $\nabla \mu_i$ include pressure gradients, the equation takes the form:

$$\sum_i n_i \nabla \mu_i - V \nabla P = 0$$

The chemical potentials of HM and NaM can be expressed by the chemical potentials of HCl, NaCl and H₂O and P by application of the Gibbs-Duhem equation and the membrane exchange equilibrium restriction, eqns. (1,2). Conversely the chemical potentials of HCl and NaCl can be expressed by the chemical potentials of HM, NaM and H₂O and P . This means that μ_1 and μ_2 are well-defined functions anywhere in the membrane even when the content of Cl⁻ ions in the membrane is negligible.

Transference numbers and diffusion coefficients. According to the Onsager reciprocal relations, $L_{ij} = L_{ji}$. The coefficient L_{44} may be interpreted as the electrolytic conductance of the membrane. The coefficients L_{14} , L_{24} and L_{34} may be identified by means of a Hittorf experiment. In the Hittorf experiment all gradients in chemical potential are equal to zero, and the following information is obtained:

$$\left(\frac{J_1}{I} \right)_{\nabla \mu_i = 0} = \frac{L_{14}}{L_{44}} = t_1 \quad (7)$$

$$\left(\frac{J_2}{I} \right)_{\nabla \mu_i = 0} = \frac{L_{24}}{L_{44}} = t_2 \quad (8)$$

$$\left(\frac{J_3}{I} \right)_{\nabla \mu_i = 0} = \frac{L_{34}}{L_{44}} = t_3 \quad (9)$$

With electrodes reversible to the Cl⁻ ion, the cation fluxes through the membrane are equal to the fluxes of the respective neutral com-

ponents through the system, $J_1 = J_{\text{HCl}} = J_{\text{H}^+}$ (in membrane) and $J_2 = J_{\text{NaCl}} = J_{\text{Na}^+}$ (in membrane). Therefore t_1 is equal to the ionic transference number of the H^+ ion, $t_1 = t_{\text{H}^+}$, and similarly $t_2 = t_{\text{Na}^+}$. The t_3 is the transference number of neutral water and does not represent any transfer of charges.

The gradient in electric potential, $\nabla\phi$, may be eliminated in the mass flux equations. The eqns. (7–9) may be substituted in eqn. (6).

$$\nabla\phi = -t_1\nabla\mu_1 - t_2\nabla\mu_2 - t_3\nabla\mu_3 - (I/L_{44}) \quad (10)$$

Substituting this expression in eqns. (3–5) gives:

$$J_1 = -(L_{11} - t_1L_{14})\nabla\mu_1 - (L_{12} - t_2L_{14})\nabla\mu_2 - (L_{13} - t_3L_{14})\nabla\mu_3 + t_1I$$

$$J_2 = -(L_{21} - t_1L_{24})\nabla\mu_1 - (L_{22} - t_2L_{24})\nabla\mu_2 - (L_{23} - t_3L_{24})\nabla\mu_3 + t_2I$$

$$J_3 = -(L_{31} - t_1L_{34})\nabla\mu_1 - (L_{32} - t_2L_{34})\nabla\mu_2 - (L_{33} - t_3L_{34})\nabla\mu_3 + t_3I$$

For convenience the equations may be written in the abbreviated form:

$$J_1 = -l_{11}\nabla\mu_1 - l_{12}\nabla\mu_2 - l_{13}\nabla\mu_3 + t_1I \quad (11)$$

$$J_2 = -l_{21}\nabla\mu_1 - l_{22}\nabla\mu_2 - l_{23}\nabla\mu_3 + t_2I \quad (12)$$

$$J_3 = -l_{31}\nabla\mu_1 - l_{32}\nabla\mu_2 - l_{33}\nabla\mu_3 + t_3I \quad (13)$$

when the current, I , is equal to zero, eqns. (11–13) represent a homogeneous set of equations with a symmetric matrix. The number of equations is reduced by one, and the number of coefficients is reduced from sixteen to nine, compared with eqns. (3–6). The diffusion coefficients l_{ij} are independent of the kind of electrodes one may use for measuring $\nabla\phi$ and independent of the transference numbers.

Eqn. (14) gives the relations between the diffusion coefficients, as obtained from pure diffusion experiments, and the phenomenological coefficients, as obtained from experiments involving mixed diffusion and electric transport.

$$l_{ij} = L_{ij} - \frac{L_{4j}L_{14}}{L_{44}} \quad i, j = 1, 2, 3 \quad (14)$$

When the Onsager reciprocal relations $L_{ij} = L_{ji}$ are valid, the relations $l_{ij} = l_{ji}$ are also valid, as can be seen from eqn. (14)

It is essential for the following derivation that all the forces in eqns. (11–13) are independent. For many kinds of membrane transports the fluxes may be interdependent. For such cases the Onsager reciprocal relations need not be valid, unless the forces are independent.⁹ We will show that the gradients in chemical potential in eqns. (11–13) can be changed independent of one another.

Application of the phase rule to the membrane-electrolyte system. Equilibrium is assumed between the membrane and the solution at the phase boundaries, in agreement with the first postulate of local equilibrium in irreversible thermodynamics. The phase rule:

$$F = C - Ph + 1 \quad (\text{at constant temperature})$$

may be applied to a region extending across a phase boundary, in order to determine the number of independent intensive variables or degrees of freedom. The number of components, C , is equal to 4, and the number of phases, Ph , is equal to 2. This gives the number of degrees of freedom, F , equal to 3. One can, e.g., change the chemical potentials μ_1 , μ_2 and μ_3 independently at both sides of the membrane, while μ_4 (μ_{HM}) and the pressure are dependent variables. Thus the potential differences $\Delta\mu_1$, $\Delta\mu_2$ and $\Delta\mu_3$ over the membrane are also independent variables.

We will now consider stationary state for the system. At any position inside the membrane, the gradients in chemical potential are then determined by the composition and the pressure of the electrolytes on the two sides of the membrane. The gradient $\nabla\mu_1$ is mainly a function of the difference $\Delta\mu_1$ over the membrane, but modified by $\Delta\mu_2$ and $\Delta\mu_3$:

$$\nabla\mu_1 = f_1(\Delta\mu_1, \Delta\mu_2, \Delta\mu_3)$$

Thus $\nabla\mu_1$ at a given position in the membrane can be changed by changing $\Delta\mu_1$, while $\nabla\mu_2$ and $\nabla\mu_3$ are kept constant by slight adjustments of $\Delta\mu_2$ and $\Delta\mu_3$. Similarly $\nabla\mu_2$ and $\nabla\mu_3$ are mainly functions of $\Delta\mu_2$ and $\Delta\mu_3$, respectively, and each can be changed independent of the others.

Transport coefficients for a cation exchange membrane. We will consider the same kind of system as discussed above. We will, however, make the restriction that the membrane is a perfect cation exchange membrane. That means

$$t_1 + t_2 = 1$$

or stated in an equivalent way

$$L_{14} + L_{24} = L_{44} \tag{15}$$

The current, I , can be expressed by the fluxes J_1 and J_2

$$I = J_1 + J_2 \tag{16}$$

Combining eqn. (16) with eqns. (11 and 12) we have

$$(l_{11} + l_{21})\nabla\mu_1 + (l_{12} + l_{22})\nabla\mu_2 + (l_{13} + l_{23})\nabla\mu_3 = 0 \tag{17}$$

This equation is valid for any value of $\nabla\mu_1$, $\nabla\mu_2$ and $\nabla\mu_3$. Because these forces are independent variables, we can conclude that

$$l_{i1} + l_{21} = 0 \quad i = 1, 2, 3 \tag{18}$$

Further, since all forces in eqns. (3–6), $\nabla\mu_1$, $\nabla\mu_2$, $\nabla\mu_3$ and $\nabla\phi$ are independent variables and since $J_1 + J_2 = I$, we obtain in a similar way:

$$L_{i1} + L_{21} = L_{41} \quad i = 1, \dots, 4 \tag{19}$$

The eqns. (19) are valid when there are three independent mass fluxes across a cation exchange membrane, and electric charge is transported by two univalent cations between electrodes reversible to a common anion. The eqns. (18) are independent of the kind of electrodes used.

The l_{ij} and L_{ij} coefficients are functions of local composition, P and T , i.e. they are gradient independent. Followingly the eqns. (18,19) are also valid for a system that is not in stationary state.

It should be noted that by assuming $L_{13} = 0$ and $\nabla\mu_3 = 0$, eqns. (3,4) become identical with the Nernst-Planck flux equation. When $L_{13} = 0$, eqns. (19) give $L_{11} = L_{14}$ and $L_{22} = L_{24}$, and the following expressions for eqns. (3,4) are obtained:

$$J_1 = -L_{14}(\nabla\mu_1 + \nabla\phi)$$

$$J_2 = -L_{24}(\nabla\mu_2 + \nabla\phi)$$

The single ion chemical potential is defined as:

$$\mu_1 = \mu_{HCl} = \mu_{H^+} + \mu_{Cl^-}$$

$$\mu_2 = \mu_{NaCl} = \mu_{Na^+} + \mu_{Cl^-}$$

With chlorine reversible electrodes, the emf of the cell, $\Delta\phi$, is defined as equal to the so-

called electric potential difference, $\Delta\psi$ minus the difference in the chemical potential of Cl^- , $\Delta\mu_{Cl^-}$, between the electrodes (two immeasurable quantities). Thus the relation between the gradients would be:

$$\nabla\phi = \nabla\psi - \nabla\mu_{Cl^-}$$

The electrochemical potential of an ion is defined:

$$\tilde{\mu}_j = \mu_j + z_j\psi \quad (z_j \text{ is the charge of the ion})$$

Using these definitions and remembering that $J_1 = J_{H^+}$ (in membrane) and $J_2 = J_{Na^+}$ (in membrane), one obtains the well-known form of the Nernst-Planck flux equation:

$$J_{H^+} = -L_{14}(\nabla\mu_{H^+} + \nabla\psi) = -L_{14}\nabla\tilde{\mu}_{H^+}$$

$$J_{Na^+} = -L_{24}(\nabla\mu_{Na^+} + \nabla\psi) = -L_{24}\nabla\tilde{\mu}_{Na^+}$$

In this way the assumptions behind the Nernst-Planck equation are shown. Assuming a zero value for L_{13} means assuming the same mobility for $\nabla\phi = 0$ and for transport in an electric field without concentration gradients. The same assumption about mobilities is inherent when the concept of electrochemical potential is used in the single ion terminology. Assuming a zero value for $\nabla\mu_3$ ($\nabla\mu_{H_2O}$) is probably close to reality for dilute aqueous solutions.

Generalization of the derivation. The above derivation can be extended to an n -component system containing ions with different charges.

For a system of n components one can choose one of the components as the reference component, thus the flux of this component is equal to zero. For an isothermal two-phase system there are $n - 1$ independent intensive variables. With an electric current passing through the system, there are n independent forces (including the gradients in chemical potential and the gradient in electric potential) and n fluxes (including the mass fluxes J_1, \dots, J_{n-1} and the electric current $J_n = I$). The fluxes may be linearly dependent:

$$\sum_{i=1}^{i=n} \alpha_i J_i = 0 \tag{20}$$

where α_i is called a coupling coefficient. The set of coupling coefficients expresses the interdependence of the fluxes. (For the system just dealt with, $HCl-NaCl-H_2O-HM$, $\alpha_1 = 1$, $\alpha_2 = 1$,

$\alpha_3=0$ and $\alpha_4=-1$. For a system HCl-CaCl₂-H₂O-HM one would have $\alpha_1=1$, $\alpha_2=2$, $\alpha_3=0$ and $\alpha_4=-1$ using a cation exchange membrane and anion reversible electrodes.)

Since all forces are independent, the phenomenological coefficients must also be linearly related:

$$\sum_{i=1}^{i=n} \alpha_i L_{ij} = 0 \quad j = 1, \dots, n \quad (21)$$

Similarly one will have for the diffusion coefficients:

$$\sum_{i=1}^{i=n-1} \alpha_i J_{ij} = 0 \quad j = 1, \dots, n-1 \quad (22)$$

The values of the coupling coefficients are determined by the selectivity of the electrodes, the selectivity of the membrane (*e.g.* cation- or anion exchange membrane) and the charges of the ions migrating through the membrane.

A set of coupling coefficients can be used to express any kind of interdependence between fluxes. Take for example the system HCl-NaCl-H₂O-HM. If all transport of water molecules is connected only to the transport of components 1 and 2, this can be expressed by eqn. (23)

$$\alpha_1 J_1 + \alpha_2 J_2 = J_3 \quad (23)$$

where α_1 and α_2 are the number of water molecules transported together with component 1 and 2, respectively. This will give eqns. (24) relating coefficients connected to transport of water:

$$\alpha_1 L_{1i} + \alpha_2 L_{2i} = L_{3i} \quad i = 1, \dots, 4 \quad (24)$$

In a set of equations describing n fluxes caused by n forces, there are n^2 coefficients. Owing to the Onsager reciprocal relations the number of independent coefficients is only $\frac{1}{2}n(n+1)$. For a system described by eqn. (20) where the n relations given in eqn. (21) are valid, the number of independent coefficients will be reduced to $\frac{1}{2}n(n-1)$. This means that $\frac{1}{2}n(n-1)$ independent transport coefficients must be determined experimentally in order to obtain a complete description of isothermal transport of mass and charge across a cation exchange membrane between anion reversible electrodes. When cation reversible electrodes are used, one will arrive at the same number of independ-

ent coefficients. This will be shown in a subsequent paper.

Commonly transport processes in membranes are described by treating the ionic species as components (see Meares *et al.*⁴ for further references). Some problems inherent in the ionic description will be discussed in a subsequent paper, where the methods will be compared.

3. EXPERIMENTAL DETERMINATION OF THE PHENOMENOLOGICAL COEFFICIENTS, L_{ij}

Experimental conditions consistent with the preceding theoretical treatment are outlined below. Returning to the previously considered example, we will discuss the experiments needed to determine six independent coefficients of a cation exchange membrane. For all the experiments the vector fluxes are assumed to be perpendicular to the surface of the membrane. This allows us to replace gradients by one-dimensional differentials in the set of flux equations (3-6). Further, the differentials are replaced by differences over a unit length of membrane thickness. The difference can be made sufficiently small to allow the use of average values for transport coefficients over the composition interval considered.

The coefficients L_{14} , L_{24} , L_{34} and L_{44} . The electrolytic conductance of the membrane, L_{44} , can be obtained by standard methods of conductance measurements. A Hittorf experiment gives either t_1 or t_2 . When L_{44} is known, L_{14} and L_{24} are obtained applying eqns. (7,8,15).

The coefficient L_{34} can be obtained in three alternative ways:

1. The coefficient L_{34} can be obtained by measuring the flux of water, J_3 , when a known current passes through the system with identical electrolytes on both sides of the membrane (electroosmosis). When L_{44} is known, L_{34} is obtained applying eqn. (9).

2. Alternatively, under the same conditions, one can measure the volume flow, J_v , which can be expressed by the equation:

$$J_v = J_1 \bar{V}_1 + J_2 \bar{V}_2 + J_3 \bar{V}_3 + I(V_{Ag} - V_{AgCl})$$

where the last term is the transfer of volume due to changes in the electrodes. The \bar{V}_i is the known molar volume of the component i in the electrolyte. When L_{44} and t_1 (and t_2) are known, one obtains the transference number for water applying eqns. (7-9), and hence $L_{34} = t_3 L_{44}$.

$$t_3 \bar{V}_3 = (J_v/I) \Delta \mu_i = 0 - (t_1 \bar{V}_1 + t_2 \bar{V}_2) - V_{Ag} + V_{AgCl}$$

3. One can obtain L_{43} and thus L_{34} by measuring the electric potential difference with identical electrolytes on both sides,

but different pressures (streaming potential). A pressure difference leads to a difference in chemical potential:

$$\Delta\mu_1 = \bar{V}_1 \Delta P \quad (25)$$

With Ag/AgCl electrodes the transfer of charge corresponds to a transfer of Ag(s) and AgCl(s) in addition to the components HCl, NaCl, H₂O. With different pressures at the two electrodes eqn. (10) is extended by the two additional components transferred:

$$\Delta\phi_{\text{obs}} = -t_1 \Delta\mu_1 - t_2 \Delta\mu_2 - t_3 \Delta\mu_3 - t_{\text{Ag}} \Delta\mu_{\text{Ag}} - t_{\text{AgCl}} \Delta\mu_{\text{AgCl}} - (I/L_{44})$$

where t_{Ag} and t_{AgCl} are defined similarly as t_1 , t_2 and t_3 , i.e. the number of moles transferred per faraday. For the present electrodes $t_{\text{Ag}} = +1$ and $t_{\text{AgCl}} = -1$, which gives:

$$\Delta\phi_{\text{obs}} = (-t_1 \bar{V}_1 - t_2 \bar{V}_2 - t_3 \bar{V}_3 - V_{\text{Ag}} + V_{\text{AgCl}}) \Delta P - (I/L_{44}) \quad (26)$$

The measurement of $\Delta\phi_{\text{obs}}$ is carried out at practically zero current, and thus one obtains:

$$(\Delta\phi_{\text{obs}}/\Delta P)_{I=0} = -t_1 \bar{V}_1 - t_2 \bar{V}_2 - t_3 \bar{V}_3 - (V_{\text{Ag}} - V_{\text{AgCl}})$$

from which t_3 can be found when all the other quantities are known, and hence $L_{34} = t_3 L_{44}$.

The coefficients L_{11} , L_{12} and L_{22} can all be obtained from a pure diffusion experiment when L_{14} , L_{24} and L_{44} are known. When I is equal to zero, eqn. (11) is reduced to:

$$J_1 = -l_{11} \Delta\mu_1 - l_{12} \Delta\mu_2 - l_{13} \Delta\mu_3$$

which combined with eqn. (18) gives:

$$J_1 = -l_{11} (\Delta\mu_1 - \Delta\mu_2) - l_{12} \Delta\mu_3 \quad (27)$$

The experiment can be arranged in such a way that $\Delta\mu_3 = 0$ (the vapour pressure over both solutions is the same), or one can correct for the small term $l_{13} \Delta\mu_3$, when measuring J_1 for known differences $\Delta\mu_1$ and $\Delta\mu_2$ which gives l_{11} . Using eqn. (14) and the known values of L_{14} , L_{24} and L_{44} , one obtains the coefficients L_{11} , L_{12} and L_{22} .

The coefficient L_{12} (the difference between L_{14} and L_{11}) is probably very small. Therefore it may be an advantage to determine this coefficient directly.

One method for direct determination of L_{12} is by means of the experiment illustrated in Fig. 2. The potential across membrane 1 is measured using electrodes reversible to H⁺. Membrane 2 (on the left hand side of the small volume) is of a very small area. This will give a high current density in the membrane, preventing H⁺ ions from diffusing to the left.

With a closed circuit, the concentrations in the small volume will change rapidly by combined diffusion and electric transport between the small and the large volume, until steady state is obtained. At steady state the electric transport of H⁺ ions across membrane 1 is just counterbalanced by the diffusion of H⁺ ions. There is no net transfer of this species, and $J_{\text{HCl}} = J_1 = 0$.

Using H⁺ reversible electrodes, the emf of the cell, $\Delta\phi'$, is equal to the sum of the following contributions:

1. The emf of the cell with Cl⁻ reversible electrodes, $\Delta\phi$, as given by eqn. (3) when $J_1 = 0$.

$$\Delta\phi = -\frac{1}{L_{14}} (L_{11} \Delta\mu_1 + L_{12} \Delta\mu_2) - \frac{L_{13}}{L_{14}} \Delta\mu_3$$

which combined with eqn. (17) gives:

$$\Delta\phi = -\Delta\mu_1 + \frac{L_{12}}{L_{14}} (\Delta\mu_1 - \Delta\mu_2) - \frac{L_{13}}{L_{14}} \Delta\mu_3$$

2. The emf of the cell H|(HCl, NaCl)_I|Cl, $\Delta\phi'' = -\mu_{\text{HCl}_I} + \text{constant}$. Here H and Cl mean electrodes reversible to H⁺ and Cl⁻, respectively, and the number I refers to the electrolyte on the left hand side of membrane 1.

3. The emf of the cell Cl|(HCl, NaCl)_{II}|H, $\Delta\phi''' = +\mu_{\text{HCl}_{II}} + \text{constant}$. The meaning of H and Cl is the same as above, and the number II refers to the electrolyte on the right hand side of membrane 1.

The emf of the cell with H⁺ reversible electrodes is then.

$$\Delta\phi' = \Delta\phi + \Delta\phi'' + \Delta\phi''' = \Delta\phi + (\mu_{\text{HCl}_{II}} - \mu_{\text{HCl}_I}) = \Delta\phi + \Delta\mu_1$$

$$\Delta\phi' = \frac{L_{12}}{L_{14}} (\Delta\mu_1 - \Delta\mu_2) - \frac{L_{13}}{L_{14}} \Delta\mu_3$$

By suitable choice of electrolyte compositions $\Delta\mu_3$, and thus the last term, can be made very small. When L_{13} and L_{14} are known, the last term can be corrected for, and L_{12} is found by measuring $\Delta\phi'$.

The coefficients L_{13} , L_{23} and L_{33} . The remaining coefficients, L_{13} , L_{23} and L_{33} can be obtained from two independent measurements of water flux.

In the pure diffusion experiment described on the basis of eqn. (27) one can measure J_3 in addition to J_1 . From eqns. (11,13,18) one obtains the ratio between the fluxes:

$$\left(\frac{J_3}{J_1}\right)_{I=0, \Delta\mu=0} = \frac{l_{31}}{l_{11}}$$

Thus l_{31} can be found after determining l_{11} . When L_{14} , L_{24} and L_{34} are known, L_{12} and L_{22} are obtained applying eqns. (14,19).

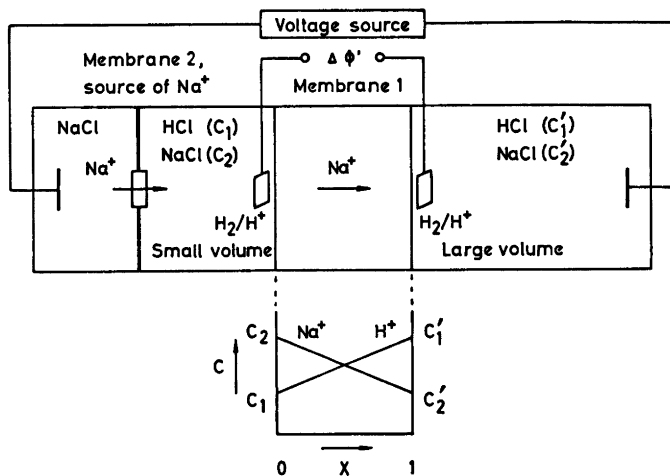


Fig. 2. Experimental arrangement for determining L_{12} . The electrodes are reversible to the H^+ ion.

The coefficients L_{13} and L_{23} may be obtained more conveniently, however, in a different way. We define two new symbols:

$$r_1 = \frac{L_{13}}{L_{14}} \quad \text{and} \quad r_2 = \frac{L_{23}}{L_{24}}$$

Introducing these symbols one obtains from eqn. (19):

$$r_1 L_{14} + r_2 L_{24} = L_{43} \quad (28)$$

or with eqns. (7,9)

$$r_1 t_1 + r_2 t_2 = t_3$$

The transference numbers t_1 and t_2 as functions of composition are known from the Hittorf experiment. From measurements of t_3 as a function of t_1 (or of composition) one can thus find r_1 and r_2 as functions of composition, yielding L_{13} and L_{23} when L_{14} and L_{24} are known.

For several systems t_3 was found to be an approximately linear function of t_1 .^{10,11} This means that r_1 and r_2 can be interpreted as a constant number of water molecules coupled to the electric transport of components 1 and 2, respectively. Eqn. (28) is the same as eqn. (24) when i is 4 and when $\alpha_1 = r_1$ and $\alpha_2 = r_2$. Thus the restriction given by eqn. (23) must lead to eqn. (28). Eqn. (28), however, involves only the electric transport of the components 1 and 2. It does not give any information about diffusional transport, and the more general eqn. (23) is not proved valid by the above experiment.

The coefficient L_{33} can be obtained by measuring the flux of water through the mem-

brane at zero current with identical electrolytes, but different hydrostatic pressure on the two sides of the membrane. The flux of water is then given by eqn. (13) combined with eqn. (25):

$$J_3 = -l_{31} \bar{V}_1 \Delta P - l_{32} \bar{V}_2 \Delta P - l_{33} \bar{V}_3 \Delta P$$

Eqn. (18) is used to eliminate l_{32} :

$$J_3 = -l_{13} (\bar{V}_1 - \bar{V}_2) \Delta P - l_{33} \bar{V}_3 \Delta P$$

A reshuffling of the above equation gives:

$$l_{33} = -\frac{1}{\bar{V}_3} \left(\frac{J_3}{\Delta P} \right) - l_{13} \left(\frac{\bar{V}_1 - \bar{V}_2}{\bar{V}_3} \right)$$

When the molar volumes, L_{13} , L_{14} , L_{34} and L_{44} are known, L_{33} is obtained by applying eqn. (14).

4. CONCLUSION

The description of transport phenomena given in this paper has several advantages:

Only measurable quantities are used for describing the transport phenomena. The mathematical description is as close to the physical processes as possible by a rigorous thermodynamic method.

The choice of components is in accordance with the phase rule. The flux equations contain independent forces, both for the case when electric energy is introduced into the system, and for the pure diffusion process.

The description is independent of the structure of the system. It can be used for non-electrolytes as well as for electrolytes. The equations are also applicable to transport of molten salts through membranes.

For a perfect cation (or anion) exchange membrane the transport coefficients are related by equations of general validity in addition to the Onsager reciprocal relations. This reduces the complexity of the system. All transport coefficients can be obtained directly from measured relations between the basic fluxes and forces.

Assumptions behind approximate flux equations can be analysed as shown by the interpretation of the Nernst-Planck flux equations. Thus the validity of the approximations can be tested experimentally.

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