

# Phenomenological Equations with Observable Electric Potentials Applied to Nonequilibrium Binary Electrolyte Solutions

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The irreversible processes which occur in a binary electrolyte solution are described by a new formalism which uses observable variables. This is based on (i) the relationship of the electrochemical potential of ion constituents to the chemical potential of the electrolyte; (ii) the notion of observable electric potential measured with reversible electrodes; and (iii) the thermodynamics of irreversible processes. The electric potential, the electric charge density, and the Nernst–Planck–Poisson formalism are reviewed in this work. The properties of the new formalism are evidenced by applying it to  $\text{MgCl}_2\text{--H}_2\text{O}$  solutions.

## Introduction

The difficulties which practical electrochemistry finds in the study of nonequilibrium systems are well-known. Most formalisms use nonobservable electric potentials, so that extra-thermodynamic assumptions are needed if one wants to relate the theory to experimental measurements. However, new ways to study these systems have been developing for several years.<sup>1–9</sup>

The way described here is based on the observable electric potential (OEP).<sup>5–9</sup> The value of this quantity at a point is the electric potential measured between a reversible electrode and another identical “reference” electrode always placed at a fixed point. The basic framework of the new formalism is the thermodynamics of irreversible processes. The phenomenological equations are deduced from the dissipation function in order to apply the Onsager reciprocal relations (ORR).<sup>10</sup>

The basic quantities of a formalism are the forces and fluxes. Here the thermodynamic forces consist of the gradients of all the electrolyte chemical potentials plus the gradient of an observable electric potential. The set of thermodynamic fluxes is formed by all but one of the ion constituent fluxes, plus the electric current density. Consequently this new formalism, all in terms of measurable quantities, helps complete the understanding of electrochemical systems provided by other formalisms.

The OEP is directly related to the electrochemical potential difference of the ion for which the two electrodes are reversible. In this theoretical sense, the OEP is not a new concept. However, it is new in the sense of an alternative to the other constructs used in irreversible thermodynamics because it is a quantity that is measured *experimentally*. Consequently it provides a formalism for transport properties which is independent of unmeasurable quantities.

A general theory of nonequilibrium electrolyte solutions using the OEP and the thermodynamics of irreversible processes has

not yet been fully achieved. Likewise a general statement about the advantages of the new formalism has not been presented. Until now it has only been applied to several special cases.<sup>5–9</sup>

One special case investigated was a ternary electrolyte solution with a common ion at uniform pressure and temperature.<sup>5</sup> There the theory was used to evaluate the OEP from both experimental data and estimates of data. However, there are insufficient data to compare the OEP measurements with experiment and thus provide a proper illustration of their use. In fact no direct OEP measurements are available for comparison in any ternary system for which all the other data are available. Moreover, an OEP in three or more component systems is complicated by the fact that it depends on the concentration distribution of the electrolytes within the solution in the cell.

In this paper, we provide in some detail the derivations and application of the new formalism to the simplest system, a binary electrolyte in a neutral solvent. The system selected for illustration,  $\text{MgCl}_2\text{--H}_2\text{O}$ , was chosen precisely because all the appropriate experimental data are available, including emf measurements which give one of the OEPs directly. In a binary system, an OEP is independent of the concentration distribution.

We will also show that a binary system has two OEPs, one for each ion constituent. Each OEP is obtained from electrodes reversible to its corresponding ion constituent.

As we will see later, this formalism is based on (i) the relationship of the electrochemical potential of ion constituents to the chemical potential of the electrolyte; (ii) the notion of observable electric potential measured with reversible electrodes; and (iii) the thermodynamics of irreversible processes. The classical decomposition of the electrochemical potential in two parts, one of chemical character and the other of electric properties, is not used here.

The phenomenological equations are deduced from the dissipation function for nonequilibrium solutions and not from Maxwell's equations of electrodynamics. Consequently we find it unnecessary to use Poisson's equation, which relates the electric charge density to the electrical potential.

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### Observable Electric Potential Formalism

Consider a system containing a solution consisting of a binary electrolyte and an unionized solvent, denoted by the subscripts *s* and *w*, respectively. Therefore, there are only two ion constituents, denoted by the subscripts 1 and 2, whose charge numbers, of opposite sign, are  $z_1$  and  $z_2$ , respectively. The stoichiometric coefficients  $\nu_1$  and  $\nu_2$  and the charge numbers are related by

$$\nu_1 z_1 + \nu_2 z_2 = 0 \quad (1)$$

One basic feature of the new formalism is the relationship between the electrochemical potential of ion constituents and the chemical potential of the electrolyte. Let  $c_i$  be the concentration of ion constituent  $i$  ( $i = 1, 2$ ) in moles per liter, and let  $\tilde{\mu}_i$  ( $i = 1, 2$ ) be the electrochemical potential of ion constituent  $i$ . When we refer these quantities to the concentration  $c_s$  and to the chemical potential  $\mu_s$  of the electrolyte, a difficulty arises. If the electroneutrality condition does not hold, the binary electrolyte is not rigorously defined at an arbitrary point in the solution. Therefore we cannot speak about a concentration and a chemical potential of the solute. This problem can be solved if we consider the following three system schemes. Let  $(c_s)_i = c_i/\nu_i$  ( $i = 1, 2$ ) be the two values for  $c_s$ , and let  $\delta c_j = c_j - \nu_j(c_s)_i$  ( $i \neq j = 1, 2$ ) be the deviation with respect to electroneutrality of the ion constituent  $j$  at a given point in the solution. At any such point, the same solution can be described by either (a) solvent plus both ion constituents  $i$  ( $i = 1, 2$ ), (b) solvent plus solute plus deviation of ion constituent 2, or (c) solvent plus solute plus deviation of ion constituent 1; i.e.,

$$(c_w c_1 c_2) \quad (2a)$$

$$(c_w (c_s)_1 \delta c_2) \quad (2b)$$

$$(c_w (c_s)_2 \delta c_1) \quad (2c)$$

Fortunately it is easy to demonstrate that the deviations  $\delta c_i$  are extremely small, so that the two values  $(c_s)_i$  ( $i = 1, 2$ ) are essentially indistinguishable from a chemical point of view.<sup>11</sup> Then if we apply Euler's equation to these system schemes, we obtain

$$\nu_1 \tilde{\mu}_1 + \nu_2 \tilde{\mu}_2 = \mu_s \quad (3)$$

where  $\mu_s$  is effectively a unique value of the chemical potential for the nearly identical concentrations  $(c_s)_1 \approx (c_s)_2$  defined above. The chemical potential  $\mu_s$  is measured through the activity coefficient  $\gamma_s$

$$\mu_s = \mu_s^* + \nu RT \ln c_s \gamma_s \quad (4)$$

where  $\nu = \nu_1 + \nu_2$  and  $\mu_s^*$  is the standard state chemical potential.

The second basic feature of the new formalism is the concept of OEP. This quantity is the electric potential measured with two identical electrodes. These identical electrodes are reversible to one of the two ion constituents of the binary system. One is placed in a certain reference point, always the same, for which we can by convention assign the OEP as zero. The other electrode is placed in any arbitrary point of the solution. The OEP is the value of the electric potential measured potentiometrically between these two electrodes.

Let the electrodes X for the chosen ion constituent be in equilibrium with the ionic species  $X^{z_1}$  of the solution; i.e.,



where  $e^-$  denotes the electron. If we assume that (i) the concentration of electrode constituents X cannot vary and (ii) the pressure and temperature are uniform, then the OEP at any point will be

$$\psi_1 = \frac{1}{z_1 F} \Delta \tilde{\mu}_1 \quad (6)$$

where as above we have taken the value of the OEP at the reference point as zero;  $F$  is Faraday's constant; and  $\Delta \tilde{\mu}_1$  is the difference in the electrochemical potential between the two points of the solution where the electrodes are placed.

Note that, under these assumptions, a change in the chemical nature of the electrodes X does not modify the measured value of these OEPs. For example, if both X electrodes are Cu (reversible to  $\text{Cu}^{2+}$ ), the measured potential is the same as if both X electrodes were Cu(Hg), both at the same amalgam composition. The "electric potential" of the solution will still be unknown, but the measured potential between the metallic phases of each pair of reversible electrodes will always give us a unique value, which will be called the OEP of  $X^{z_1}$ .

Since the binary electrolyte solutions have two ion constituents, there must be two OEPs, one for each. Thus the second OEP is measured with electrodes reversible to the other ion species  $Y^{z_2}$ . The OEP associated with  $Y^{z_2}$  will be different from that for  $X^{z_1}$  but will be independent of the chemical nature of the Y electrode pair. For the gradients of the two OEPs we deduce in a general form

$$\nabla \tilde{\mu}_i = z_i F \nabla \psi_i \quad i = 1, 2 \quad (7)$$

This result shows the simplicity of the formalism: the gradients in the OEP are the gradients in the electrochemical potentials divided by the constant quantity  $z_i F$  and can be measured with any kind of electrodes reversible to species  $i$  ( $i = 1, 2$ ). We must remember that the system is at uniform pressure and temperature; under other conditions eq 7 has more terms. From eq 3 we obtain a relationship between the two OEPs:

$$\nabla \psi_1 - \nabla \psi_2 = \frac{1}{\nu_1 z_1 F} \nabla \mu_s \quad (8)$$

The third part of the new formalism is the irreversible thermodynamics. If thermal equilibrium and uniform pressure are assumed, the dissipation function  $T\sigma$  in our system is given by<sup>10,12</sup>

$$T\sigma = - \sum_{i=1}^2 \mathbf{j}_i \nabla \tilde{\mu}_i \quad (9)$$

where  $\mathbf{j}_i$  is the flow density of matter of the ion constituent  $i$  in a solvent-fixed frame of reference.

The local nonequilibrium state in the solution is described by the pair of driving forces  $(\nabla \tilde{\mu}_1, \nabla \tilde{\mu}_2)$ ; but there are other ways to express the irreversibility. From eqs 3 and 7 we can obtain

$$\nabla \tilde{\mu}_2 = z_2 F \nabla \psi_2 \quad (10)$$

$$\nabla \tilde{\mu}_1 = \frac{1}{\nu_1} \nabla \mu_s + z_1 F \nabla \psi_2 \quad (11)$$

and therefore we see that  $(\nabla \mu_s, \nabla \psi_2)$  is an equivalent pair of driving forces. The fluxes conjugate to the new forces  $(\mathbf{j}_1/\nu_1, \mathbf{i})$

are deduced from the dissipation function, which can now be written as

$$T\sigma = -\frac{1}{\nu_1} \mathbf{j}_1 \nabla \mu_s - \mathbf{i} \nabla \psi_2 \quad (12)$$

where  $\mathbf{i} = F(z_1 \mathbf{j}_1 + z_2 \mathbf{j}_2)$  is the electric current density. The phenomenological equations become

$$\frac{1}{\nu_1} \mathbf{j}_1 = -\lambda_{11} \nabla \mu_s - \lambda_{1\psi} \nabla \psi_2 \quad (13)$$

$$\mathbf{i} = -\lambda_{\psi 1} \nabla \mu_s - \lambda_{\psi\psi} \nabla \psi_2 \quad (14)$$

When we use the OEP  $\psi_1$ , the analogous equations are

$$T\sigma = -\frac{1}{\nu_2} \mathbf{j}_2 \nabla \mu_s - \mathbf{i} \nabla \psi_1 \quad (15)$$

$$\frac{1}{\nu_2} \mathbf{j}_2 = -\lambda_{22} \nabla \mu_s - \lambda_{2\psi} \nabla \psi_1 \quad (16)$$

$$\mathbf{i} = -\lambda_{\psi 2} \nabla \mu_s - \lambda_{\psi\psi} \nabla \psi_1 \quad (17)$$

with forces  $(\nabla \mu_s, \nabla \psi_1)$  and fluxes  $(\mathbf{j}_2/\nu_2, \mathbf{i})$ .

The phenomenological coefficients  $\lambda_{ij}$  ( $i, j = 1, 2, \psi$ ) are related to the three following experimental transport quantities: the specific electric conductance  $\kappa$ , the Hittorf transference numbers  $t_i$ , and the diffusion coefficient  $D$  in the solvent-fixed frame<sup>12</sup>. From the phenomenological equations we deduce<sup>5</sup>

$$\lambda_{\psi\psi} = \kappa \quad (18)$$

$$\lambda_{i\psi} = \lambda_{\psi i} = \frac{t_i \kappa}{\nu_i z_i F} \quad i = 1, 2 \quad (19)$$

$$\lambda_{ii} = \frac{D}{\partial \mu_s / \partial c_s} + \frac{t_i^2 \kappa}{\nu_i^2 z_i^2 F^2} \quad i = 1, 2 \quad (20)$$

Here we have assumed that ORR hold. If an ORR test is considered,<sup>12</sup> then the phenomenological coefficients will be given in terms of emf transference numbers  $t_i^c$  and Hittorf transference numbers  $t_i^h$

$$\lambda_{i\psi} = \lambda_{\psi i} = \frac{t_i^h \kappa}{\nu_i z_i F} \quad i = 1, 2 \quad (21)$$

$$\lambda_{\psi i} = \frac{t_i^c \kappa}{\nu_i z_i F} \quad i = 1, 2 \quad (22)$$

It is of course possible to relate the  $\lambda_{ik}$  based on the OEP to the customary ionic Onsager coefficients<sup>10,12</sup> based on ionic fluxes and on forces consisting of their corresponding electrochemical potentials  $\nabla \tilde{\mu}_i$ . In a matrix notation, the new and customary older<sup>10,12</sup> forces and fluxes can be written

$$\mathbf{X}^{(j)} = (\nabla \mu_s, \nabla \psi_j) \quad j = 1, 2 \quad (23)$$

$$\mathbf{J}^{(j)} = \left( \frac{1}{\nu_i} \mathbf{j}_i, \mathbf{i} \right) \quad i \neq j = 1, 2 \quad (24)$$

$$\mathbf{X} = (\nabla \tilde{\mu}_1, \nabla \tilde{\mu}_2) \quad (25)$$

$$\mathbf{J} = (\mathbf{j}_1, \mathbf{j}_2) \quad (26)$$

These are related through

$$\mathbf{X} = \mathbf{X}^{(j)} \mathbf{M}^{(j)} \quad j = 1, 2 \quad (27)$$

$$\mathbf{J}^{(j)} = \mathbf{J}(\mathbf{M}^{(j)})^T \quad j = 1, 2 \quad (28)$$

where

$$\mathbf{M}^{(1)} = \begin{pmatrix} 0 & \frac{1}{\nu_2} \\ z_1 F & z_2 F \end{pmatrix} \quad (29)$$

$$[\mathbf{M}^{(1)}]^{-1} = \begin{pmatrix} \nu_1 & \frac{1}{z_1 F} \\ \nu_2 & 0 \end{pmatrix} \quad (30)$$

$$\mathbf{M}^{(2)} = \begin{pmatrix} \frac{1}{\nu_1} & 0 \\ z_1 F & z_2 F \end{pmatrix} \quad (31)$$

$$[\mathbf{M}^{(2)}]^{-1} = \begin{pmatrix} \nu_1 & 0 \\ \nu_2 & \frac{1}{z_2 F} \end{pmatrix} \quad (32)$$

We have employed the superscript T for the transposed matrix.

The phenomenological coefficient matrices  $\mathbf{L}$  and  $\lambda^{(j)}$  of

$$\mathbf{J} = -\mathbf{X} \mathbf{L}^T \quad (33)$$

$$\mathbf{J}^{(j)} = -\mathbf{X}^{(j)} (\lambda^{(j)})^T \quad j = 1, 2 \quad (34)$$

are related by

$$\lambda^{(j)} = \mathbf{M}^{(j)} \mathbf{L} (\mathbf{M}^{(j)})^T \quad j = 1, 2 \quad (35)$$

Consequently

$$\lambda_{ii} = \frac{1}{\nu_i^2} l_{ii} \quad i = 1, 2 \quad (36)$$

$$\lambda_{i\psi} = \lambda_{\psi i} = \frac{z_1 l_{i1} + z_2 l_{i2}}{\nu_i} F \quad i = 1, 2 \quad (37)$$

$$\lambda_{\psi\psi} = \sum_{i=1}^2 \sum_{j=1}^2 z_i z_j l_{ij} F^2 \quad (38)$$

where  $l_{ij}$  ( $i, j = 1, 2$ ) are the customary phenomenological coefficients.<sup>10,12</sup> Thus these  $\lambda_{ij}$  ( $i, j = 1, 2, \psi$ ) can be calculated either from tabulated  $l_{ij}$  by eqs 36–38 or directly from experimental data by eqs 18–20.

A related formalism was presented by Førlund et al. several years ago.<sup>1–4</sup> They work with the same thermodynamic forces, but the fluxes involved are different: they use electrolyte fluxes, and we work with ion constituent fluxes. We feel that when  $\mathbf{i} \neq 0$ , it is not possible to define electrolyte fluxes.

Frequently the phenomenological equations are desired in terms of concentration gradients. From eqs 13–17, we deduce

$$\frac{1}{\nu_i} \mathbf{j}_i = -D_i^{(j)} \nabla c_s - \frac{t_i \kappa}{\nu_i z_i F} \nabla \psi_j \quad i, j = 1, 2 \quad (39)$$

$$\mathbf{i} = -A^{(j)} \nabla c_s - \kappa \nabla \psi_j \quad j = 1, 2 \quad (40)$$

where  $D_i^{(j)}$  and  $A^{(j)}$  are given by

$$D_i^{(j)} = D + \frac{t_i t_k \kappa}{\nu_i \nu_k z_i z_k F^2} \frac{\partial \mu_s}{\partial c_s} \quad i, j = 1, 2 \quad (41)$$

$$A^{(j)} = \frac{t_j \kappa}{\nu_j z_j F} \frac{\partial \mu_s}{\partial c_s} \quad i \neq j = 1, 2 \quad (42)$$

In eq 41, if  $i \neq j$ , we take  $k = i$ ; and if  $i = j$ , we take  $k \neq i$ . From eqs 39 and 40 we obtain the “superposition” result

$$\frac{1}{\nu_i} \mathbf{j}_i = -D \nabla c_s + \frac{t_i}{\nu_i z_i F} \mathbf{i} \quad i = 1, 2 \quad (43)$$

which is also obtained in the customary formalism.<sup>12</sup> Pure diffusion occurs when  $\mathbf{i} = 0$ . In this case the electrolyte diffuses as a whole, and the electrolyte flux will be  $\mathbf{j}_s = \mathbf{j}_i/\nu_i$  ( $i = 1, 2$ ).

### Other Formalisms

There are other formalisms which describe nonequilibrium electrolyte solutions with other electric potentials. Two ways have been developed to define the electric potential: (i) by splitting into two terms the electrochemical potential  $\tilde{\mu}_i = \mu_i + z_i F \phi$  ( $i = 1, 2$ ), where  $\mu_i$  is the chemical potential and (ii) by applying the Nernst–Planck–Poisson (NPP) formalism.

In the first way, the definition must be completed by postulating the Nernst potential of the electrodes  $\Delta \mu_i / z_i F$ . In Table 1 we give the three most common proposals; these postulate the ion activity coefficient in different ways. Thus, we obtain three different electric potentials  $\phi_i$  ( $i = 1, 2, m$ ), characterized by the subscript  $i$ . These electric potential gradients are related to the OEP gradients by

$$\nabla \phi_i = \nabla \psi_i - \frac{RT}{z_i F} \nabla \ln c_s \quad i = 1, 2 \quad (44)$$

$$\nabla \phi_m = \nabla \psi_i - \frac{1}{\nu_i z_i F} \nabla \mu_s \quad i = 1, 2 \quad (45)$$

where the subscript  $m$  refers to the mean activity coefficient of the electrolyte  $\gamma_s$ .

Using eqs 39 and 40 and 44–45, we deduce the following phenomenological equations

$$\frac{1}{\nu_i} \mathbf{j}_i = -\delta_i^{(j)} \nabla c_s - \frac{t_i \kappa}{\nu_i z_i F} \nabla \phi_j \quad i = 1, 2; j = 1, 2, m \quad (46)$$

$$\mathbf{i} = -\alpha^{(j)} \nabla c_s - \kappa \nabla \phi_j \quad j = 1, 2, m \quad (47)$$

where  $\delta_i^{(j)}$  and  $\alpha^{(j)}$  are given by

$$\delta_i^{(j)} = D_i^{(j)} + \frac{RT t_i \kappa}{\nu_i z_i z_j F^2} \quad i, j = 1, 2 \quad (48)$$

$$\delta_i^{(m)} = D_i^{(i)} + \frac{t_i \kappa}{\nu \nu_i z_i^2 F^2} \frac{\partial \mu_s}{\partial c_s} \quad i = 1, 2 \quad (49)$$

$$\alpha^{(j)} = A^{(j)} + \frac{RT \kappa}{z_j c_s F} \quad j = 1, 2 \quad (50)$$

$$\alpha^{(m)} = A^{(j)} + \frac{\kappa}{\nu z_j F} \frac{\partial \mu_s}{\partial c_s} \quad j = 1, 2 \quad (51)$$

The  $\phi_i$  ( $i = 1, 2$ ) are also the quasi-electrostatic potentials which were studied by Newman.<sup>13,14</sup>

**TABLE 1: Proposals for Defining Three Electric Potentials  $\phi_i$  by Postulating the Ion Activity Coefficients  $\gamma_i$**

$\gamma_i$	$\nabla \mu_i$	$\phi$
$\gamma_1 = 1$	$\nabla \mu_1 = RT \nabla \ln c_s$	$\phi_1$
$\gamma_2 = 1$	$\nabla \mu_2 = RT \nabla \ln c_s$	$\phi_2$
$\gamma_1 = \gamma_2 = \gamma_s$	$\nabla \mu_1 = \nabla \mu_2 = \frac{1}{\nu} \nabla \mu_s$	$\phi_m$

We now consider the NPP formalism. Here the fluxes are expressed by<sup>13</sup>

$$\mathbf{j}_i^* = -D_i^* \nabla c_i - z_i u_i F c_i \nabla \psi^* + c_i \mathbf{v} \quad i = 1, 2 \quad (52)$$

where  $\mathbf{j}_i^*$  are the fluxes in the apparatus-fixed reference frame;  $D_i^*$  are the diffusion coefficients of the ionic species;  $u_i$  are the ionic mobilities;  $\psi^*$  is the NPP electric potential in the solution; and  $\mathbf{v}$  is the bulk velocity. Here  $c_i$  ( $i = 1, 2$ ) denote the ionic concentrations. The Nernst–Einstein equation  $D_i^* = RT u_i$  will be assumed.

When the link with the NPP formalism is considered, it is necessary to assume the following: (i) the electrolyte is completely dissociated (then  $c_i$  ( $i = 1, 2$ ) also expresses the ion constituent concentration); (ii) the ion constituent fluxes are  $\mathbf{j}_i^* - c_i \mathbf{v} \approx \mathbf{j}_i$ ;<sup>15</sup> and (iii) when  $\nabla c_s = 0$  the NPP phenomenological equations will be identical to the phenomenological equations of other formalisms. Then the NPP phenomenological equations will be

$$\frac{1}{\nu_i} \mathbf{j}_i = -D_i^* \nabla c_s - z_i u_i F c_s \nabla \psi^* \quad i = 1, 2 \quad (53)$$

$$\mathbf{i} = -A^* \nabla c_s - \kappa \nabla \psi^* \quad (54)$$

where

$$A^* = \nu_i z_i (D_i^* - D_j^*) F \quad i \neq j = 1, 2 \quad (55)$$

$$u_i = \frac{t_i \kappa}{\nu_i c_s z_i^2 F^2} \quad i = 1, 2 \quad (56)$$

From eqs 53 and 54 we deduce

$$\frac{1}{\nu_i} \mathbf{j}_i = -D^* \nabla c_s + \frac{t_i}{\nu_i z_i F} \mathbf{i} \quad i = 1, 2 \quad (57)$$

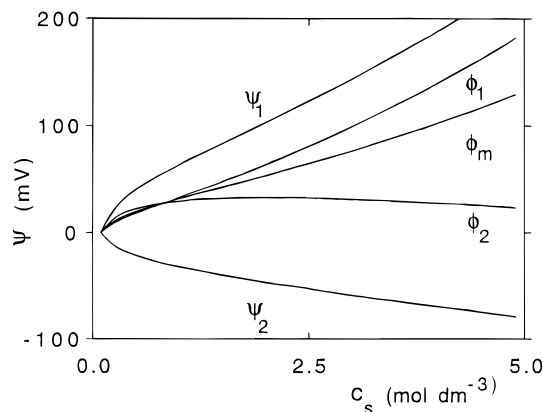
where the diffusion coefficient  $D^*$  will be

$$D^* = D_1^* t_2 + D_2^* t_1 \quad (58)$$

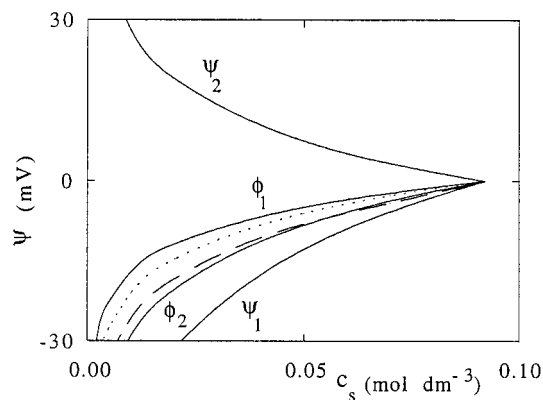
### MgCl<sub>2</sub> + H<sub>2</sub>O Solutions

We now apply the different formalisms described above to the system MgCl<sub>2</sub> + H<sub>2</sub>O. When working electrodes are excluded, the electric current density will be effectively zero at every point, i.e.,  $i = 0$ . Under these conditions we deduce from eq 40 that, in a nonequilibrium binary solution, the difference in the value of the OEP between two points depends exclusively on their solute concentrations, and not on the concentration profile between them, as has been well confirmed.<sup>16</sup> (For two or more solutes, the OEP does depend on the concentration profiles.<sup>5</sup>) Therefore functions of the kind  $\psi_i = \psi_i(c_s)$  ( $i = 1, 2$ ) and  $\phi_i = \phi_i(c_s)$  ( $i = 1, 2, m$ ) can be deduced. This is done below for MgCl<sub>2</sub> + H<sub>2</sub>O solutions at 25 °C. The subscripts 1 and 2 denote the ion constituents Mg and Cl, respectively.

In Figure 1 we show these functions from 0.092 to 4.9 mol dm<sup>-3</sup>. The  $\psi_2 = \psi_2(c_s)$  are the emf values given in Table II by Phang and Stokes<sup>17</sup> for concentration cells with transference.



**Figure 1.** Electric potentials in solutions from 0.092 to 4.9 mol dm<sup>-3</sup> when  $i = 0$ . Values of  $\psi_2$  from Phang and Stokes.<sup>17</sup>



**Figure 2.** Electric potentials in solutions from 0.0001 to 0.092 mol dm<sup>-3</sup> when  $i = 0$ . Data from Miller et al.<sup>20</sup> (—)  $\psi^*$ ; (···)  $\phi_m$ .

We assign a reference value  $\psi_2 = 0$  at  $c_s = 0.092$  mol dm<sup>-3</sup>. To deduce  $\psi_1 = \psi_1(c_s)$ , we use eq 8 cast in terms of activity coefficients

$$d\psi_1 = d\psi_2 + \frac{\nu RT}{\nu_1 z_1 F} d \ln m_s \gamma_s^{(m)} \quad (59)$$

The  $\ln m_s \gamma_s^{(m)}$  values given by Rard and Miller<sup>18</sup> are transformed from molality  $m_s$  quantities to molarity  $c_s$  quantities.<sup>19,20</sup> The functions  $\phi_i = \phi_i(c_s)$  ( $i = 1, 2, m$ ) are deduced from eqs 44 and 45.

Six electric potentials from 0.0001 to 0.0920 mol dm<sup>-3</sup> are shown in Figure 2. To deduce  $\psi_2 = \psi_2(c_s)$ , we use eq 40, i.e.,

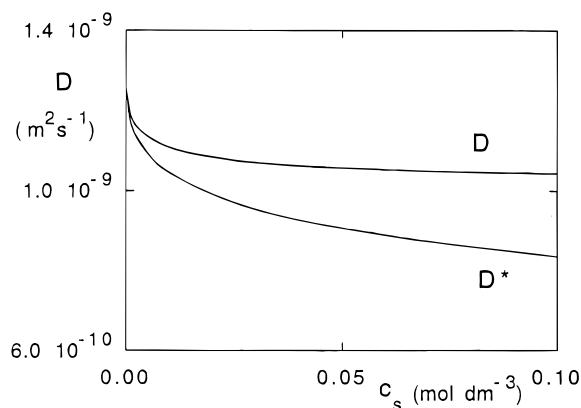
$$d\psi_2 = -\frac{\nu RT}{\nu_1 z_1 c_s F} t_1 \left( 1 + \frac{d \ln \gamma_s^{(c)}}{d \ln c_s} \right) dc_s \quad (60)$$

and as we are working with dilute solutions we can assume that

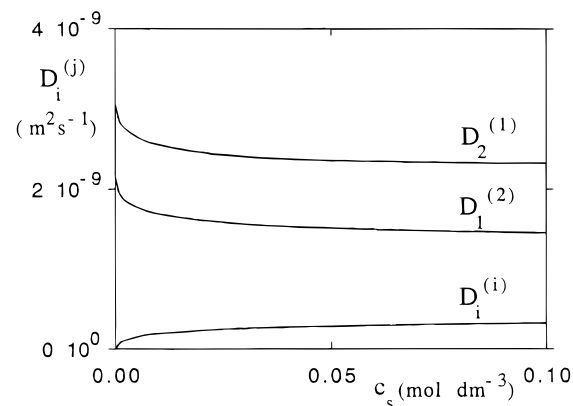
$$\left( 1 + \frac{d \ln \gamma_s^{(c)}}{d \ln c_s} \right) \approx \left( 1 + \frac{d \ln \gamma_s^{(m)}}{d \ln m_s} \right) \quad (61)$$

The data given in Table V of Miller et al.<sup>20</sup> are used. Then we obtain  $\psi_1 = \psi_1(c_s)$  and  $\phi_i = \phi_i(c_s)$  ( $i = 1, 2, m$ ) as before. We also include in Figure 2 the electric potential  $\psi^*$  used in the NPP formalism, which we obtain from eq 54, i.e.,

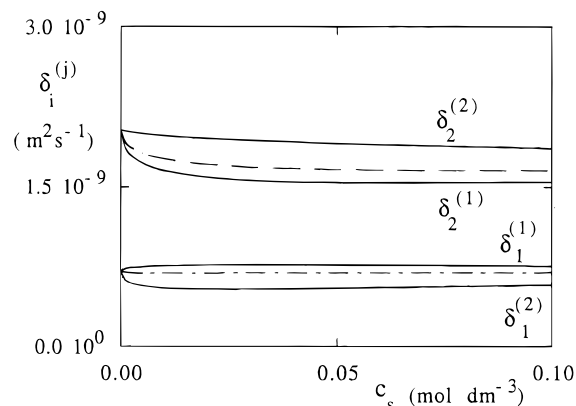
$$d\psi^* = \frac{RT}{Fc_s} \left( t_2 - \frac{t_1}{2} \right) dc_s \quad (62)$$



**Figure 3.** Diffusion coefficients  $D$  and  $D^*$  of the electrolyte. Data from Miller et al.<sup>20</sup>



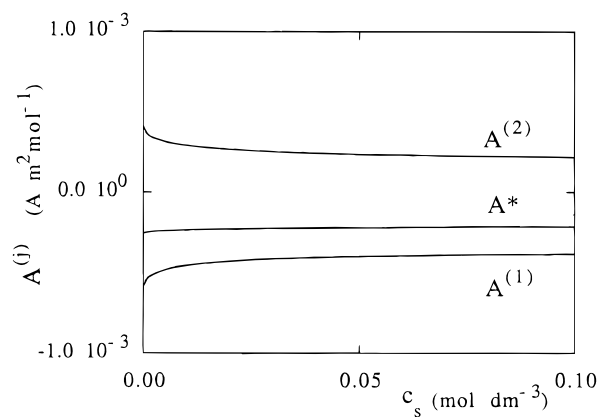
**Figure 4.** Coefficients  $D_i^{(j)}$  ( $i, j = 1, 2$ ) of eqs 40. Data from Miller et al.<sup>20</sup>



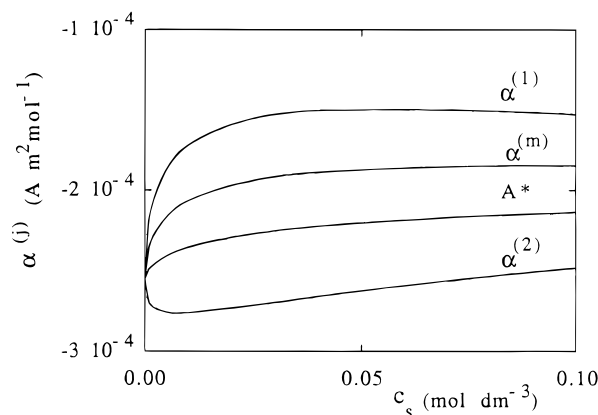
**Figure 5.** Coefficients  $\delta_i^{(j)}$  ( $i = 1, 2; j = 1, 2, m$ ) of eqs 47. Data from Miller et al.<sup>20</sup> (—)  $\delta_2^{(m)}$ ; (— · —)  $\delta_1^{(m)}$ .

Figures 1 and 2 show important differences between the electric potential–concentration functions. When  $c_s \rightarrow 0$ , all the electric potentials go to  $\pm\infty$ . Thus the electric potential gradients in very dilute solutions can easily reach very high values. Fortunately this is compensated by the extremely small values of the specific electric conductance  $\kappa$ . From the results in Figure 2 we can deduce the corresponding liquid junction potential (ljv) between two solutions  $c_s'$  and  $c_s''$ . Usually this quantity is given by the difference in  $\phi_i$  ( $i = 1, 2, m$ ) or  $\psi^*$ . According to the electric potential chosen, we obtain very different values.

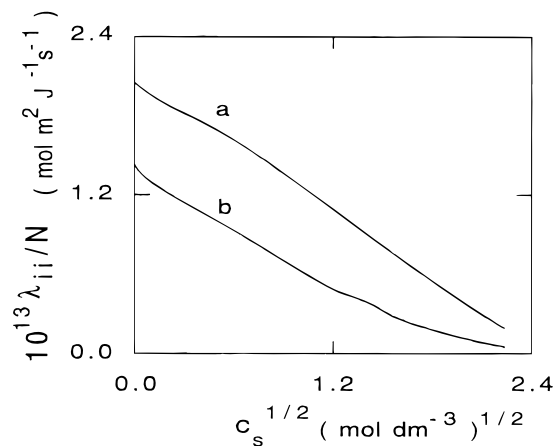
Figures 3–7 show the phenomenological coefficients for dilute solutions obtained from the data in Table V of Miller et al.<sup>20</sup> We also assume the approximation of eq 61. We emphasize that Figure 4 shows that  $D_i^{(i)} \ll D_i^{(j)}$  ( $i \neq j = 1, 2$ ); therefore, the terms  $D_i^{(j)} \nabla c_s$  in eqs 39 have very different values



**Figure 6.** Coefficients  $A^{(j)}$  ( $j = 1, 2$ ) and  $A^*$  of eqs 41 and 55. Data from Miller et al.<sup>20</sup>



**Figure 7.** Coefficients  $\alpha^{(j)}$  ( $j = 1, 2, m$ ) of eqs 48. Data from Miller et al.<sup>20</sup> The values of  $A^*$  of eq 55 have also been included.



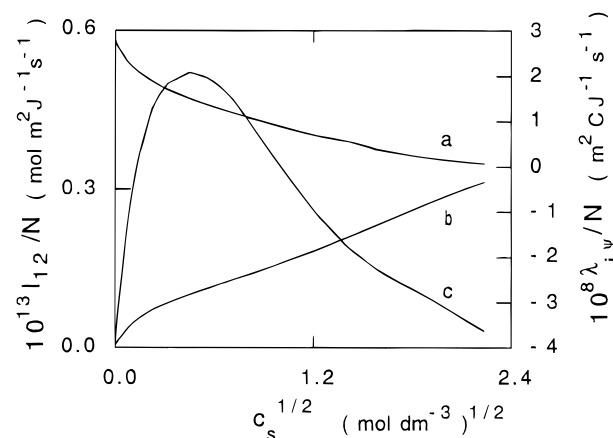
**Figure 8.** Coefficients  $\lambda_{22}/N$  (a) and  $l_{11}/N = \lambda_{11}/N$  (b). Data from Miller et al.<sup>20</sup>  $N$  is the normality in equiv  $\text{dm}^{-3}$ .

according to  $i \neq j$  or  $i = j$  ( $i, j = 1, 2$ ). We see also that for highly dilute solutions  $D_i^{(j)} \rightarrow 0$  ( $i = 1, 2$ ). In Figure 5 we see that  $\delta_i^{(j)} \rightarrow \delta_i$  ( $i = 1, 2; j = 1, 2, m$ ) when  $c_s \rightarrow 0$ ; this quantity is expressed by

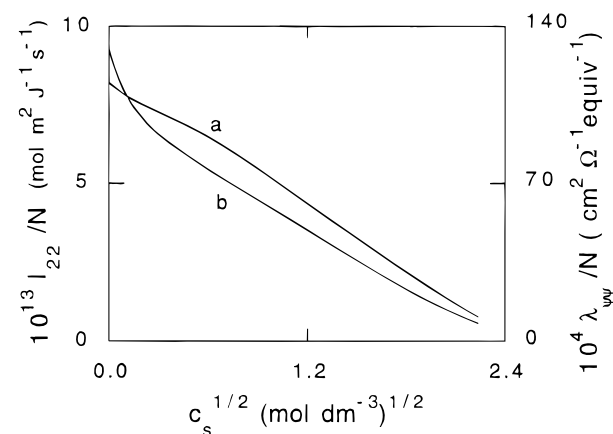
$$\delta_i = D + \frac{RTt_i\kappa}{v_i^2 z_i^2 c_s F^2} (v t_i - v_k) \quad (i \neq k = 1, 2) \quad (63)$$

Figure 7 shows that all  $\alpha^{(j)} \rightarrow A^*$  ( $j = 1, 2, m$ ) when  $c_s \rightarrow 0$ .

Figures 8–10 show the coefficients  $l_{ij}/N$  ( $i, j = 1, 2$ ) and  $\lambda_{ij}/N$  ( $i, j = 1, 2, \psi$ ) for the solution  $\text{MgCl}_2 + \text{H}_2\text{O}$  at 25 °C up to 5.0  $\text{mol dm}^{-3}$ .  $N$  is the normality in equiv  $\text{dm}^{-3}$ . The values of the ionic transport coefficients  $l_{ij}/N$  ( $i, j = 1, 2$ ) have been



**Figure 9.** Coefficients  $\lambda_{1\psi}/N$  (a),  $\lambda_{2\psi}/N$  (b), and  $l_{12}/N$  (c). Data from Miller et al.<sup>20</sup>



**Figure 10.** Coefficients  $l_{22}/N$  (a) and  $\lambda_{\psi\psi}/N$  (b). Data from Miller et al.<sup>20</sup>

taken from Table VI of Miller et al.<sup>20</sup> and the  $\lambda_{ij}/N$  obtained from them using eqs 36 and 37. Division of  $l_{ij}$  and  $\lambda_{ij}$  by  $N$  reduces significantly their change with concentration.

## Discussion

The phenomenological equations proposed above consider a linear dependence between the forces and fluxes, as is usually accepted when solution transport processes are studied. In particular, they apply very well in electrolyte solutions for large values of the forces. As shown above, the experimental values of the phenomenological coefficients can be evaluated from experimental values of the classical coefficients  $t_i$ ,  $\kappa$ , and  $D$ .

The new formalism uses the concept of ion constituents. Since it is independent of the degree of dissociation of the electrolyte, it can be applied to both strong or weak electrolytes at all values of solute concentrations, just as can the customary formalism.<sup>10,12,13</sup>

There are differences in the number of independent coefficients of the various formalisms. The new and customary formalisms compute their phenomenological coefficients from the three experimental transport quantities  $t_i$ ,  $\kappa$ , and  $D$ , together with the solute activity coefficient, an equilibrium property. Consequently they are both exact and complete. In contrast the NPP equations evaluate their coefficients from only the two transport quantities  $t_i$  and  $\kappa$  and consequently are an incomplete and inexact approximation. More specifically, the NPP equations are fundamentally a dilute solution approximation which omits the cation–anion cross-terms.

A relationship between the electric potential and the electric charge density  $\rho = F \sum z_i c_i$ , such as Poisson's equation, is not

proposed in the new formalism. We noted above that the phenomenological equations have been deduced from the dissipation function and not from Maxwell's laws. The  $\nabla\psi_i$  ( $i = 1, 2$ ),  $\nabla\phi_i$  ( $i = 1, 2, m$ ), and  $\nabla\psi^*$  values depend on  $\nabla c_s$  and  $\mathbf{i}$  through the phenomenological coefficients. The values that  $\rho$  can reach have little interest. However, we can evaluate  $\rho$  if we assume a value for  $\rho_0$  at the initial time  $t_0$  and then compute the change through  $d\rho = -\nabla\mathbf{i} \cdot d\mathbf{t}$ .<sup>21-23</sup>

Finally we contrast this new  $\lambda_{ij}$  formalism with the customary  $l_{ij}$  formalism. The new one has the advantage of being formulated from the start with measurable quantities and also of using the electric current density as one of the fluxes, but the disadvantage that the numerical values of the transport properties of the solution  $\lambda_{ij}$  depend on whether the electrodes are reversible to ion 1 or to ion 2. The customary one has the advantage that the values of the solution transport properties  $l_{ij}$  are independent of any electrodes, but the disadvantage that the formulation begins with unmeasurable quantities. However, the description of any real experiment in the customary formalism always results in the combination of the unmeasurable properties to form measurable ones.<sup>10,12</sup> We also note that these "unmeasurable quantities" are considered unmeasurable because currently there is no practical experimental way to obtain them. However, in principle they could be obtained experimentally if it were possible to measure the rise time of the potential in the  $10^{-9}$  s just after the formation of the boundary in a concentration cell with transference.<sup>22</sup>

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## References and Notes

- (1) Førland, K. S.; Førland, T. *J. Stat. Phys.* **1995**, 78, 513.
- (2) Førland, K. S.; Førland, T.; Ratkje, S. K. *Acta Chem. Scand. A* **1977**, 31, 47.
- (3) Førland, K. S.; Førland, T.; Ratkje, S. K. *Advances in Thermodynamics*; Taylor and Francis: New York, 1992; Vol. 6, p 340.
- (4) Førland, K. S.; Førland, T.; Ratkje, S. K. *Irreversible Thermodynamics: Theory and Applications*; John Wiley: New York, 1988.
- (5) Garrido, J.; Compañ, V.; López, M. L. *J. Phys. Chem.* **1994**, 98, 6003.
- (6) Garrido, J.; Mafé, S.; Aguilera, V. M. *Electrochim. Acta* **1988**, 33, 1151.
- (7) Garrido, J.; Compañ, V.; Aguilera, V. M.; Mafé, S. *Electrochim. Acta* **1990**, 35, 705.
- (8) Garrido, J.; Compañ, V. *J. Phys. Chem.* **1992**, 96, 2721.
- (9) Garrido, J.; Compañ, V.; López, M. L. *Electrochim. Acta* **1993**, 38, 877.
- (10) Haase, R. *Thermodynamics of Irreversible Processes*; Dover: New York, **1990**; p 293.
- (11) Guggenheim, E. A. *Thermodynamics*; North-Holland: Amsterdam, 1967; p 299.
- (12) Miller, D. G. *J. Phys. Chem.* **1966**, 70, 2639.
- (13) Newman, J. *Electrochemical Systems*; Prentice-Hall: London, 1973; pp 76 and 217.
- (14) Smyrl, W. H.; Newman, J. *J. Phys. Chem.* **1968**, 72, 4660.
- (15) We remember that  $\mathbf{v} = \sum \mathbf{j}_i^*$ . When  $\mathbf{i} = 0$  we know that  $\mathbf{v} = V_s \mathbf{j}_s^* + V_w \mathbf{j}_w^*$ , and we obtain  $\mathbf{j}_i^* - c_i \mathbf{v} = c_w V_w \mathbf{j}_i \approx \mathbf{j}_i$ . This also requires  $c_s$  to be relatively small, corresponding to fairly dilute solutions.
- (16) Brown, A. S.; MacInnes, D. A. *J. Am. Chem. Soc.* **1935**, 57, 1356.
- (17) Phang, S.; Stokes, R. H. *J. Solution Chem.* **1980**, 9, 497.
- (18) Rard, J. A.; Miller, D. G. *J. Chem. Eng. Data* **1981**, 26, 38.
- (19) Dunlop, P. J.; Gosting, L. J. *J. Phys. Chem.* **1959**, 63, 86.
- (20) Miller, D. G.; Rard, J. A.; Eppstein, L. B.; Albright, J. G. *J. Phys. Chem.* **1984**, 88, 5739.
- (21) Hafemann, D. R. *J. Phys. Chem.* **1965**, 69, 4226.
- (22) Leckey, J. H.; Horne, F. H. *J. Chem. Phys.* **1981**, 85, 2504.
- (23) Mafé, S.; Pellicer, J.; Aguilera, V. M. *J. Phys. Chem.* **1986**, 90, 6045.