THE CHARGE SEPARATION PROCESS IN NON-HOMOGENEOUS ELECTROLYTE SOLUTIONS *

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ABSTRACT

The charge separation process occurring in two different solutions of the same electrolyte brought into contact is studied using Poisson's equation and the (simplified) equations of transport. The process is characterized on the basis of the change in observable physical magnitudes. The relevance of the "diffusional" and "electric" relaxations is analysed. The results obtained can be applied to problems of ionic transport across membranes and liquid junctions, and contribute to the study of the transport of charged matter during the time interval in which the "charge" plays a significant role. Although, unfortunately the time domain involved in the electric relaxation seems to be inaccessible to precise experimental measurement, the physical model provides a detailed description of the way charge separation takes place. The latter is consistent with experimental observations at "large times".

An equation for the current density has been obtained from the ionic transport equations and Poisson's equation. By using the former, it has been shown that the classical treatment by Planck (commonly used for describing the diffusion potential in ionic transport through membranes) implies neglecting the whole charge separation process (assuming $\tau_e \simeq 0$, where τ_e is the electric relaxation time). The inconsistencies involved in this have been shown.

Finally, the significance of the two terms ("conduction" and "displacement" current) in the equation for the total current density is discussed. Both terms play an important role in ionic transport processes through totally or partially blocked interfaces.

(I) INTRODUCTION

It is intended in this paper to describe the charge separation process taking place when two solutions of the same binary electrolyte at different concentrations are brought into contact. It is well known that under certain boundary conditions the system formed by the two solutions reaches a steady state of material transport. This steady state can be characterized by observable magnitudes, e.g. the salt flux.

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* Dedicated to Salva Navarro (deceased June 1986).

Our aim is to characterize the nature of the steady state reached from the viewpoint of the charge transport. This objective requires solving the ionic flux equations and Poisson's equation in the so-called "charge-controlled" time domain ($t \sim 10^{-9}$ s [1,2]).

The problem of solving Nernst–Planck and Poisson equations is not trivial [1–4]. In a relatively simple way, using some approximations, calculations have been made here for the time evolution of the electric potential difference between the two solutions and for the ionic fluxes through a fictitious contact plane between them. The results obtained can be applied to problems of ionic transport across membranes and liquid junctions, and contribute to the study of charged matter transport during the time interval in which "charge" plays a dominant role.

The scheme of this paper is as follows. First, the relation between Poisson's equation and the equation for the electric current is discussed. Next follows a brief analysis of the classical hypotheses concerning the electric charge along the transport zone: the "electroneutrality" (ELC) and "constant field" (GCF) assumptions. The inconsistencies arising when the time scale associated with the charge rearrangement is ignored are discussed later and the necessity of taking into account those time scales for a rigorous analysis of the process is demonstrated.

After establishing the transport problem we describe the technique employed to solve it as well as the results obtained: the time evolution of the electric potential difference, the ionic fluxes and the electric current density. The way these magnitudes change shows how, after the first time interval ($t \simeq 10^{-9}$ s), ion fluxes couple with each other so that an electroneutral salt flux results.

(II) THE CLASSICAL HYPOTHESES

The time variation of charge density, $\rho(x, t)$, over the transport zone arising between two electrolyte solutions at different concentrations has been described classically by Poisson's equation:

$$\partial^2 \phi(x, t) / \partial x^2 = -\rho(x, t)/\epsilon \tag{1}$$

where ϕ stands for the electric potential and ϵ for the dielectric constant of the medium, x and t having their usual meaning. More recent studies [1,5–7] replace eqn. (1) by the so-called equation for the electric current I (for the sake of simplicity, we call it "current" though strictly speaking I stands for an electric current density):

$$I = F \sum_{i}^{n} z_i J_i - \epsilon \frac{\partial^2 \phi}{\partial x \partial t} \tag{2}$$

Equation (2) was originally introduced by Cohen and Cooley [8]; z_i and J_i are the charge number and the flux of ion i, respectively, and n is the number of ionic species present. Before attempting our analysis, we will discuss the relationship between eqns. (1) and (2).

Buck [1] has recently reported a derivation of eqn. (2). We are going to prove, by an alternative procedure to that of Buck, that eqn. (2) is already implicitly included in the system formed by the transport equations and Poisson's equation. To do this, consider the continuity equation for the transport of material between both solutions:

$$\frac{\partial c_i}{\partial t} = -\frac{\partial J_i}{\partial x} \qquad i = 1, 2, , \ldots, n \tag{3}$$

where c_i stands for the molar concentration of species i. Multiplying eqns. (3) by $z_i F$ and summing them all up, one easily obtains the continuity equation for charge transport:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}\left\{F\sum_i^n z_i J_i\right\} = 0 \qquad \rho \equiv F\sum_i^n z_i c_i \tag{4}$$

Equation (4) can be rewritten, using eqn. (1), as:

$$\frac{\partial}{\partial x}\left\{F\sum_i^n z_i J_i - \epsilon\frac{\partial^2 \phi}{\partial x\,\partial t}\right\} = 0 \tag{5}$$

Equation (5) suggests, by *analogy* to the purely electrodynamic case considered by Maxwell [9], that the total current I can be defined as

$$I \equiv I_q + I_d \qquad \text{(see eqn. 2)} \tag{6}$$

where I_d is a term analogous to the electrodynamic displacement current. Note that in the purely electrodynamic case, charges move exclusively under the influence of electric fields. However, the problem we deal with here is the transport of "charged matter", its motion being due to both the electric potential gradient and the concentration gradient. The relevance of this fact will become apparent through this paper.

Since eqn. (6) can be derived from eqn. (1), the latter will be employed in our treatment. (A discussion about the meaning of I_q and I_d in this problem will be provided later.)

The electric charge behaviour over the transport zone has been described classically by means of two approximations to eqn. (1): ELC and GCF. These assumptions were proposed by Planck and Goldman, respectively. These authors also formulated the conditions under which such hypotheses should be used (see, for example, refs. 10 and 11). ELC establishes that, to a good approximation, the ionic concentrations verify the relationship

$$\sum_i^n z_i c_i = 0 \tag{7}$$

everywhere in the transport zone; GCF assumes the electric field to be constant over this region:

$$\partial \phi/\partial x = \text{constant} \tag{8}$$

The consistency of eqns. (7) and (8) with eqn. (1) has usually been explained involving the quotient (L_D/d), where L_D is the Debye length of the system, $L_D = (\epsilon RT/F^2 c_0)^{1/2}$, and d is the diffusion zone thickness. In the last expression, c_0 stands for a typical concentration of the problem ("scaling concentration") and the constants R, T and F have their usual meaning.

By using perturbation [12,13] and numerical [14] treatments, it has been shown previously that eqn. (1) tends to eqn. (7) when $(L_D/d) \ll 1$. However, for $(L_D/d) \to 1$, eqn. (1) becomes eqn. (8). In fact, this result follows immediately from a simple order-of-magnitude analysis. To show this, let us write eqn. (1) as

$$\left| \frac{\partial^2 \phi}{\partial x^2} \right| \sim 10^{16} \quad (\text{V cm/mol}) \cdot \Delta c \quad (\text{mol/cm}^3) \tag{9}$$

where it is assumed that $F \simeq 10^5$ C/mol and $\epsilon \sim 10^{-11}$ C/V cm. Δc denotes the "excess" of ions (either positive or negative) present in a certain volume over the diffusion zone. Now consider the cases:

(a) $d \gg L_D$

Suppose, for example, that $d = 10^{-2}$ cm. The, $|\partial\phi/\partial x| \sim RT/Fd = 2.6$ V/cm. From eqn. (9) and by integrating $\partial^2\phi/\partial x^2$ between $x = 0$ and $x = d$, one gets

$$\frac{\left| \left(\frac{\partial\phi}{\partial x} \right)_{x=d} - \left(\frac{\partial\phi}{\partial x} \right)_{x=0} \right|}{d} \sim 10^{16} \left\{ \frac{1}{d} \int_0^d \Delta c \ dx \right\} \equiv 10^{16} \, \overline{\Delta c} \tag{10}$$

Hence, for a 10% change in $(\partial\phi/\partial x)$ over a diffusion zone of $d = 10^{-2}$ cm, a "mean excess" of $\overline{\Delta c} = 10^{-16} (0.26/10^{-2}) \sim 10^{-15}$ mol/cm^3 is needed.

(b) $d \sim L_D$

Suppose $d = 10^{-7}$ cm. Then $|\partial\phi/\partial x| \sim 2.6 \times 10^5$ V/cm. From eqn. (10) and proceeding as in the above case, a "mean excess" of $\overline{\Delta c} = 10^{-5}$ mol/cm^3 is required for a 10% change in $(\partial\phi/\partial x)$ over d.

In (a), differences of only 10^{-15} mol/cm^3 can cause a significant change in the electric field. However, in the mathematical limit $d \to L_D$ (case b), the electric fields become so strong and the distances are so small that significant changes in $(\partial\phi/\partial x)$ with x call for $\overline{\Delta c}$ of the same order of magnitude as that of the scaling electrolyte concentration of the problem. Obviously, this is not feasible and the electric field is nearly constant along the diffusion zone [14].

An interesting chapter of physical chemistry concerning transport in electrolyte solutions is devoted to the problem of consistency between eqns. (7), (8) and eqn. (1). As a matter of fact, even solving the transport equations by using the ELC assumption, a non-zero net charge density (a "residual charge", see refs. 2, 10 and 15) is obtained finally. The problem becomes harder if we notice that, under certain conditions [11,16], the solution obtained when using eqn. (8) is "exact", i.e. provided

that these conditions are met, a strictly zero ρ is found everywhere in the diffusion zone. What would then be the origin of the steady potential difference observed experimentally in these cases [11,16]?

The answer may be given as follows. The charge separation process requires times τ_e of the order of 10^{-9} s, and it begins over spatial regions L_D of the order of 10^{-7} cm (just over the "sharp" zone of contact between the two solutions). It can be assumed (as usual) that at the time we make our analysis, the system has already reached a "steady state" concerning the transport of material across a given zone of thickness $d \gg L_D$ (e.g. a membrane). However, the problem is that we have not considered the *way* the system develops in order to reach that state. In other words, the inconsistencies mentioned would arise only when considering times of the order of the diffusion relaxation time τ_d ($\tau_d \sim 10$ s if $d = 10^{-2}$ s), implicitly taking $\tau_e \cong 0$. This amounts to ignoring the entire charge separation process between the two solutions (see Appendix 1). Describing this phenomenon is just the aim proposed here.

(III) FORMULATION OF THE PROBLEM

The problem of charge separation in non-homogeneous electrolyte solutions has been studied by Hafemann [17] using digital simulation techniques. His results provide the variation of $\rho(x, t)$ and the potential difference $\Delta\phi(t)$ with time; they were obtained by numerical solution of the transport equations and Poisson's equation (in its integral form). MacGillivray [18] solved Nernst–Planck and Poisson equations (in a time-dependent scheme), and remarked on both the difficulty and the interest concerned with the time interval in which charge separation occurs. However, a specific analytical solution of the problem was not given until Jackson's studies [19]. His analysis is also restricted to the magnitudes $\rho(x, t)$ and $\Delta\phi(t)$, and conclusions are drawn very clearly. Perhaps a more complete analysis is that reported recently by Leckey and Horne [7] (analytical-numerical). The present paper tackles the problem in a similar way to the latter article.

The situation analysed is shown in detail in Fig. 1. Two solutions of the same binary electrolyte at different concentrations are brought into contact at the mid-point $x = x_0$ at $t = 0$. The absolute values of the ionic concentrations are assumed to be small enough so that the transport equations can be approximated by Nernst–Planck flux equations [1]. (Thus, cross-term effects are omitted and activity coefficients are taken to be unity approximately.) Solvent flux is assumed to be negligible. The transport coefficients (the ionic diffusion coefficients, D_i, in this case) and the dielectric constant ϵ are considered to be constant along the diffusion zone (reasonable approximations due to hypothesis 2 in Fig. 1). There are no externally applied electric fields.

On the assumptions made above, the boundary conditions can be expressed in the following way:

$$J_i(0, t) = J_i(d, t) = 0 \qquad i = 1, 2 \tag{11}$$
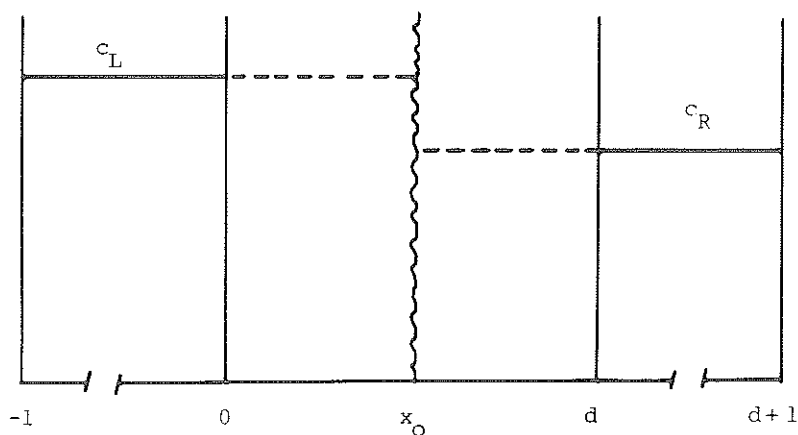
$$1. \quad 1 >> d >> L_D \qquad\qquad 3. \quad t < \tau_d = (2/\pi^2)\,[d^2/(D_1+D_2)]$$

$$2. \quad |c_L - c_R|/c_R << 1 \qquad 4. \quad x = x_0 \cong d/2, \quad t = 0$$

Fig. 1. Schematic representation of the transport problem considered. At the instant $t = 0$, two solutions of the same binary electrolyte at different concentrations ($c_{L,R}$) are brought into contact at a central point x_0 (4). The difference in the concentrations is small compared with their absolute values (2). Two bulk containers, large compared with the diffusion zone thickness (e.g. a simple, porous membrane of thickness d) are located on its two sides (1). As usual, the thickness of the zone through which transport occurs is much greater than the Debye length typical of the problem (1). The analysis is carried out for times smaller than the diffusional relaxation time τ_d (3), because we are interested in the charge separation process, and this involves times $\tau_e \equiv [\epsilon RT/F^2 c_0 (D_1 + D_2)] \ll \tau_d$ [1,2]. This allows it to be assumed that the fluxes across the interfaces placed at $x = 0$ and $x = d$ are nearly zero, since ions need about τ_d s to migrate from $x = x_0$ to both interfaces.

$$\phi(0, t) = 0 \qquad \frac{\partial \phi}{\partial x}(0, t) = 0 \tag{12}$$

(since $0 = \int_0^d \rho(x, t)\,dx = -\epsilon\{\partial\phi(d, t)/\partial x - \partial\phi(0, t)/\partial x\} \to \partial\phi(d, t)/\partial x = 0$); eqns. (11) and (12) yield

$$\frac{\partial c_i(0, t)}{\partial x} = \frac{\partial c_i(d, t)}{\partial x} = 0 \qquad i = 1, 2 \tag{13}$$

$$c_i(x, 0) = \begin{cases} c_L = c_0 + \delta c_0/2 & 0 < x < x_0 \\ c_R = c_0 - \delta c_0/2 & x_0 < x < d \end{cases} \quad (\delta c_0 \ll c_0) \quad i = 1, 2 \tag{14}$$

If we substitute the transport equations into the mass conservation eqns. (3), we get

$$\frac{\partial c_i}{\partial t} = D_i \left\{ \frac{\partial^2 c_i}{\partial x^2} + (-1)^{i-1} \frac{F}{RT} \left\{ \frac{\partial c_i}{\partial x} \frac{\partial \phi}{\partial x} + c_i \frac{\partial^2 \phi}{\partial x^2} \right\} \right\} \qquad i = 1, 2 \tag{15}$$

where $z_1 = -z_2 = 1$ is assumed. Since $\delta c_0/c_0 \ll 1$, we can write $c_i(x, t) = c_0 + p_i(x, t)$, $p_i(x, t) \ll c_0$. Using this expression and Poisson's eqn. (1), eqn. (15) becomes:

$$\frac{\partial p_i}{\partial t} = D_i \left\{ \frac{\partial^2 p_i}{\partial x^2} + (-1)^{i-1} \frac{F}{RT} \left[\frac{\partial p_i}{\partial x} \frac{\partial \phi}{\partial x} - \frac{F}{\epsilon}(c_0 + p_i)(p_1 - p_2) \right] \right\}$$

$$\simeq D_i \left\{ \frac{\partial^2 p_i}{\partial x^2} + (-1)^i \left(F^2 c_0/\epsilon RT \right)(p_1 - p_2) \right\} \qquad i = 1, 2 \qquad (16)$$

where the condition $p_i \ll c_0$ has been used, which allows for linearizing the equations. The next step is to solve eqns. (16) under boundary conditions (11)–(14).

(IV) SOLUTION

A solution technique previously described by Malvadkar and Kostin [20] has been employed here. Take in our case

$$c_i(x, t) = c_0 + \sum_{m=1}^{\infty} a_{im} b_{im}(t) \cos\left\{ \frac{m\pi x}{d} \right\} \qquad (17)$$

for the solution of eqns. (16), now rewritten in the form

$$\partial_t p_1 = D_1 \left\{ \partial_x^2 p_1 - (L_D)^{-2}(p_1 - p_2) \right\}$$
$$\partial_t p_2 = D_2 \left\{ \partial_x^2 p_2 + (L_D)^{-2}(p_1 - p_2) \right\} \qquad (18)$$

Then by separating the variables and taking into account eqns. (13) and (14), one obtains

$$b_{im}(t) = (2S_m)^{-1} \left\{ \left[(-1)^i (D_1 - D_2) + (D_1 + D_2)\alpha_m + S_m \right] \exp\left(-t/\tau_m^1 \right) \right.$$

$$\left. + \left[(-1)^{i-1}(D_1 - D_2) - (D_1 + D_2)\alpha_m + S_m \right] \exp\left(-t/\tau_m^2 \right) \right\} \qquad i = 1, 2$$

$$S_m = \left[4D_1 D_2 \alpha_m^2 + (D_1 - D_2)^2(1 + \alpha_m)^2 \right]^{1/2}$$

$$\alpha_m = (d/L_D)^2 (1/\pi m)^2$$

$$\left(\tau_m^i \right)^{-1} = \tfrac{1}{2}(m\pi/d)^2 \left[(D_1 + D_2)(1 + \alpha_m) + (-1)^i S_m \right] \qquad i = 1, 2 \qquad (19)$$

The coefficients a_{im} can be calculated from the initial boundary conditions by means of the orthogonality property of the cosine function. For the distribution in Fig. 1, the following is obtained:

$$a_{im} = (2/\pi m)(c_L - c_R) \sin(m\pi x_0/d) \qquad i = 1, 2 \qquad (20)$$

(the equality $a_{1m} = a_{2m}$ results from the fact that both solutions are electrically neutral at $t = 0$).

So far, we have applied the technique by Malvadkar and Kostin [20]. Next we will apply approximations 1–4 (see Fig. 1) to the solution (17) + (19)–(20).

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(V) APPROXIMATIONS

The term a_{im} is essentially proportional to $1/m$, which suggests that the series (17) might be truncated. A preliminary question is to study the dependence of $b_{im}(t)$ on m. Since α_m is proportional to $(1/m^2)$, this study can be made in terms of α_m. Consider the cases:

(I) $\alpha_m \ll 1$ $(m\pi \gg d/L_D$, i.e. "large" m, as follows from 1 in Fig. 1)
Then by taking $S_m \simeq (D_1 - D_2)$, one gets $(\tau_m^i)^{-1} \simeq m^2/\tau_{dj}$ $(i \neq j)$, where $\tau_{di} \equiv d^2/\pi^2 D_i$ $(i,\ j = 1, 2)$. Therefore, it readily follows from eqn. (19) that $b_{im}(t) \sim \exp(-m^2 t/\tau_{di})$.

(II) $\alpha_m \gg 1$ $(m\pi \ll d/L_D$, i.e. "small" m)
Now $S_m \simeq (D_1 + D_2)\alpha_m + ((D_1 - D_2)^2/(D_1 + D_2))$. If the D_is are not very different (NaCl, KCl), $S_m \cong (D_1 + D_2)\alpha_m$. Then

$$\frac{1}{\tau_m^i} \simeq (1/2\alpha_m L_D^2)(D_1 + D_2)\left\{(1 + \alpha_m) + (-1)^i \alpha_m\right\}$$

$$= \begin{cases} (D_1 + D_2)/2\alpha_m L_D^2 \equiv m^2/\tau_d & \tau_d \equiv d^2/\pi^2(D_1 + D_2) & i = 1 \\ (D_1 + D_2)/2\alpha_m L_D^2[1 + 2\alpha_m] & \\ \quad \equiv m^2/\tau_d + 1/\tau_e & \tau_e \equiv [\epsilon RT/F^2(D_1 + D_2)c_0] & i = 2 \end{cases}$$

Thus

$$b_{im}(t) \simeq \exp(-t/\tau_m^1) + \frac{(-1)^{i-1}}{2\alpha_m}[(D_1 - D_2)/(D_1 + D_2)]$$
$$\times [\exp(-t/\tau_m^2) - \exp(-t/\tau_m^1)] \sim \exp(-m^2 t/\tau_d) \tag{21}$$

Hence, at a given time t, $b_{im}(t)$ decreases exponentially as m^2 increases in both cases. Since a_{im} decreases as $1/m$, the first terms of the series (17) may be regarded as a first approximation (assumption II).

On the other hand, the hypothesis $d \gg L_D$ plays a relevant role in our procedure. It relies upon the nature of the phenomenon itself: $d \sim 10^{-2}$ cm and $L_D \sim 10^{-7}$ cm are typical values. Since $\alpha_m = (d/L_D)^2(1/\pi m)^2$, it seems reasonable, on the above facts, to take $\alpha_m \gg 1$ in our treatment, thus justifying the approximation (21).

In order to evaluate the maximum number of terms that can contribute to the sum (17), let us consider $\alpha_m \gtrsim 1$ which constitutes the limit of validity of the assumption (II). Then one would get

$$m \leq E[d/\pi L_D] \tag{22}$$

where $E[x]$ denotes "the integer part of x". As we have accepted assumption (II), eqn. (22) should be regarded as an *upper limit* in our formalism. Its meaning will be discussed later.

By using the approximations (21), the solution (17) can be rewritten as

$$
c_i(x,\ t) = c_0 + \frac{2}{\pi}(c_L - c_R)\left\{ \sum_{m=1}^{N} \frac{\sin\!\left(\dfrac{m\pi x_0}{d}\right)\cos\!\left(\dfrac{m\pi x}{d}\right)}{m}\ \exp\!\left(-m^2 t/\tau_d\right) \right.
$$

$$
\left. \times \left[1 + \frac{(-1)^{i-1}}{2\alpha_m}\frac{D_1 - D_2}{D_1 + D_2}\left(\exp(-t/\tau_e) - 1\right)\right]\right\} \tag{23}
$$

and then, from eqn. (21),

$$
c_i(x,\ t) \simeq c_0 + \frac{2}{\pi}(c_L - c_R)\sum_{m=1}^{N}\frac{\sin\!\left(\dfrac{m\pi x_0}{d}\right)\cos\!\left(\dfrac{m\pi x}{d}\right)}{m}\ \exp\!\left(-m^2 t/\tau_d\right) \tag{24}
$$

where the series has been truncated at a given term N ($N < E[d/\pi L_D]$ at the most), owing to assumption (II). From eqn. (23) we obtain

$$
c_1(x,\ t) - c_2(x,\ t) = 2\frac{(c_L - c_R)}{d}L_D^2\frac{D_1 - D_2}{D_1 + D_2}
$$

$$
\times\left\{\sum_{m=1}^{N}\sin\!\left(\frac{m\pi x_0}{d}\right)\cos\!\left(\frac{m\pi x}{d}\right)\!\left(\frac{m\pi}{d}\right)\exp\!\left(-m^2 t/\tau_d\right)\right\}
$$

$$
\times\left(\exp(-t/\tau_e) - 1\right) \tag{25}
$$

Then

$$
\frac{\partial \phi}{\partial x}(x,\ t) = -\frac{F}{\epsilon}\int_0^x (c_1 - c_2)\,\mathrm{d}y = -\left(\frac{2RT}{Fc_0}\right)\!\left(\frac{c_L - c_R}{d}\right)\!\frac{D_1 - D_2}{D_1 + D_2}
$$

$$
\times\left\{\sum_{m=1}^{N}\sin\!\left(\frac{m\pi x_0}{d}\right)\sin\!\left(\frac{m\pi x}{d}\right)\exp\!\left(-m^2 t/\tau_d\right)\right\}\!\left(\exp(-t/\tau_e) - 1\right) \tag{26}
$$

The physical meaning of assumption (II) will become clear later. Nevertheless, a first interpretation can be given from eqns. (18). Indeed, as the system approaches the steady state, $\partial_t p_i \to 0$. Therefore, taking into account eqn. (24), eqn. (18) leads to (see Appendix 2):

$$
\frac{|p_1 - p_2|}{p_i} \sim \left[\frac{L_D}{d}\right]^2 \tag{27}
$$

Equation (27) implies that after a certain time has elapsed, the system develops in such a way that the net charge at any point over the diffusion zone is much smaller than the ionic concentrations there (provided that $d \gg L_D$). Therefore, the undoubted relevance of the ELC assumption, formulated by Planck in 1889 for the steady state, is confirmed.

(VI) RESULTS

(VI.1) Liquid junction potential

We denote by the above name the electric potential difference that arises between the two electrolyte solutions,

$$\Delta\phi_t \equiv \phi(d,\,t) - \phi(0,\,t) = \int_0^d (\partial\phi/\partial x)\,\mathrm{d}x$$

$$= -\frac{F}{\epsilon}\int_0^d \mathrm{d}x \int_0^x \mathrm{d}y\big(c_1(y,\,t) - c_2(y,\,t)\big) = \frac{2RT}{\pi F c_0}\frac{D_1 - D_2}{D_1 + D_2}(c_L - c_R)$$

$$\times\left\{\sum_{m=1}^N \frac{\sin\!\left(\dfrac{m\pi x_0}{d}\right)}{m}\exp\big(-m^2 t/\tau_d\big)\int_0^d \mathrm{d}x\,\frac{m\pi}{d}\left(-\sin\!\left(\frac{m\pi x}{d}\right)\right)\right\}\big(\exp(-t/\tau_e) - 1\big)$$

$$= \frac{4RT}{\pi F}\frac{D_1 - D_2}{D_1 + D_2}\frac{c_L - c_R}{c_0}\left\{\sum_{m=1}^N \frac{\sin\!\left(\dfrac{m\pi x_0}{d}\right)\sin^2\!\left(\dfrac{m\pi}{2}\right)}{m}\exp\big(-m^2 t/\tau_d\big)\right\}$$

$$\times\big(1 - \exp(-t/\tau_e)\big) \tag{28}$$

Let us take $x_0 = d/2$. In addition, we are interested in the time interval involved in the charge separation process, $0 < t \sim \tau_e \ll \tau_d$ (usually $\tau_d \sim 10^9\ \tau_e$); so we have $\exp(-m^2 t/\tau_d) \simeq 1$. Therefore,

$$\Delta\phi_t \simeq \frac{4RT}{\pi F}\frac{D_1 - D_2}{D_1 + D_2}\frac{\delta c_0}{c_0}\left\{\sum_{m=1}^N \frac{\sin^3\!\left(\dfrac{m\pi}{2}\right)}{m}\right\}\big(1 - \exp(-t/\tau_e)\big)$$

$$\simeq \frac{RT}{F}\frac{D_1 - D_2}{D_1 + D_2}\frac{\delta c_0}{c_0}\big(1 - \exp(-t/\tau_e)\big) \tag{29}$$

since $[\sum_{m=1}^N \sin^3(m\pi/2)/m] \simeq \pi/4$. (Note that $N < 10^4$, from eqn. 22.) The term $\sin(m\pi x_0/d)$ in eqn. (28) actually depends on the mid-point x_0. Note that if, instead of taking $x_0 \simeq d/2$ in eqn. (28), we estimate the contribution of the sine function to the sum in the following way:

$$\overline{\sin\!\left(\frac{m\pi x_0}{d}\right)} \equiv \frac{1}{d}\int_0^d \mathrm{d}x_0\,\sin(m\pi x_0/d) = 2\sin^2(m\pi/2)/m\pi \tag{30}$$

we get the same result as that of eqn. (29). Indeed,

$$\frac{4}{\pi}\frac{2}{\pi}\left[\sum_{m=1}^N \sin^4\!\left(\frac{m\pi}{2}\right)\Big/m^2\right] \simeq \frac{8}{\pi^2}\frac{\pi^2}{8} = 1$$

Now in the situation outlined in Fig. 1, $d \gg L_D$, and then the liquid junction

potential $\Delta\phi_P$ obtained by Planck (with the ELC assumption) for the steady state is excellent [2,19]:

$$\Delta\phi_P = -\frac{RT}{F}\frac{D_1-D_2}{D_1+D_2}\ln\frac{c_R}{c_L} = \frac{RT}{F}\frac{D_1-D_2}{D_1+D_2}\ln\left(1+\frac{\delta c_0}{c_0}\right)$$

$$\simeq \frac{RT}{F}\frac{D_1-D_2}{D_1+D_2}\frac{\delta c_0}{c_0} \tag{31}$$

By comparing eqns. (29) and (31) we have

$$\Delta\phi_t \simeq \Delta\phi_P\left(1-\exp(-t/\tau_e)\right) \qquad 0 < t \sim \tau_e \tag{32}$$

This result is in qualitative agreement with earlier analyses based on different techniques: Hafemann's [17], digital simulation; Jackson's [19], perturbative analysis; Mafé et al.'s [2], numerical and order-of-magnitude analysis. Leckey and Horne have also shown the role times of the order of $\tau_e \sim 10^{-9}$ s play in the development of the steady liquid junction potential.

On the other hand, if, following Guggenheim [21], we admit that Planck's analysis is concerned with a steady-state liquid junction potential which is not dependent on d, provided that the thickness d is artificially maintained constant (e.g. by means of a membrane), then Planck's steady state is reached for $t \gg \tau_e$. That is, Planck ignored in his formalism times shorter than those associated with the establishment of $\Delta\phi_P$, which amounts to writing $\tau_e \simeq 0$. This fact (which is proved in Appendix 1) leads to the inconsistencies mentioned at the beginning of this paper.

(VI.2) Electric charge density

From eqn. (25) it turns out that $\rho(x, t)$ may be written as

$$\rho(x, t) = F(c_1 - c_2) = 2\pi\frac{\epsilon RT}{Fd^2}\frac{c_L - c_R}{c_0}\frac{D_1-D_2}{D_1+D_2}$$

$$\times\left\{\sum_{m=1}^{N} m\sin\left(\frac{m\pi}{2}\right)\cos\left(\frac{m\pi x}{d}\right)\exp\left(-m^2 t/\tau_d\right)\right\}\left(\exp(-t/\tau_e)-1\right)$$

$$\simeq -\frac{\epsilon RT}{Fc_0}\frac{D_1-D_2}{D_1+D_2}\frac{\partial^2 c_i}{\partial x^2}\left(\exp(-t/\tau_e)-1\right) \tag{33}$$

The connection between eqn. (33) and the expression for the net charge density in Planck's formalism is not straightforward because the latter is not referred to a diffusion zone meeting exactly the conditions stated in our case. However, if we consider $t \gg \tau_e$ (or we assume that $\tau_e = 0$) in eqn. (33), $\exp(-t/\tau_e) \simeq 0$, and the resulting expression can be compared, concerning orders of magnitude, with the "residual charge density" of Planck [2,10]:

$$\rho(x) = \frac{\epsilon RT}{F}\frac{D_1-D_2}{D_1+D_2}\frac{d^2\ln c_i}{dx^2} \qquad c_i = c_L + \frac{c_R-c_L}{d}x \tag{34}$$

Yet eqn. (33) verifies the charge conservation law

$$\int_0^d \rho(x, t)\, dx = 0 \tag{35}$$

while expression (34) does not verify this law [10]. Once again, we see that ignoring what occurs in the charge separation time domain leads to inconsistencies as far as $\rho(x, t)$ is concerned.

(VI.3) Ionic fluxes

Ionic fluxes are calculated from the Nernst–Planck equation simply by substituting $c_i(x, t)$ (eqn. 23) and $\partial\phi/\partial x$ (eqn. 26) in it. Then one obtains

$$J_i(x, t) \simeq J_{i0} P(x, t)\left\{ 1 + (-1)^{i-1} \frac{D_1 - D_2}{D_1 + D_2}\left[1 + \frac{2}{\pi} \frac{c_L - c_R}{c_0} U(x, t) \right]\right.$$

$$\left. \times \left(\exp(-t/\tau_e) - 1\right)\right\} \qquad i = 1, 2 \tag{36}$$

where

$$J_{i0} \equiv -2D_i(c_R - c_L)/d \qquad i = 1, 2$$

$$P(x, t) \equiv \sum_{m=1}^{N} \sin\left(\frac{m\pi x_0}{d}\right) \sin\left(\frac{m\pi x}{d}\right) \exp\left(-m^2 t/\tau_d\right)$$

$$U(x, t) \equiv \sum_{m=1}^{N} \frac{\sin\left(\dfrac{m\pi x_0}{d}\right) \cos\left(\dfrac{m\pi x}{d}\right)}{m} \exp\left(-m^2 t/\tau_d\right) \tag{37}$$

Since $(c_L - c_R)/c_0 = \delta c_0/c_0 \ll 1$, we can make the approximation

$$J_i(x, t) \simeq J_{i0} P(x, t)\left\{ 1 + (-1)^{i-1} \frac{D_1 - D_2}{D_1 + D_2}\left(\exp(-t/\tau_e) - 1\right)\right\}$$

$$= \begin{cases} J_0 P(x, t)\left[1 + \dfrac{D_1 - D_2}{2D_2} \exp(-t/\tau_e)\right] & i = 1 \\[2ex] J_0 P(x, t)\left[1 - \dfrac{D_1 - D_2}{2D_1} \exp(-t/\tau_e)\right] & i = 2 \end{cases}$$

$$J_0 \equiv -2D_M(c_R - c_L)/d \qquad D_M \equiv 2D_1 D_2/(D_1 + D_2) \tag{38}$$

Assume that $x_0 \simeq d/2$. Then at the contact point between the two solutions one gets

$$P(d/2, t) = \sum_{k=0}^{N/2} \exp\left(-(2k+1)^2 t/\tau_d\right)$$

$$U(d/2, t) = 0 \tag{39}$$

whence

$$J_i(d/2,\ t) = J_0 \left(\sum_{k=0}^{N/2} \exp\left(-(2k+1)^2 t/\tau_d\right) \right)$$

$$\times \left[1 + (-1)^{i-1} \frac{D_1 - D_2}{2D_{3-i}} \exp(-t/\tau_e) \right] \quad i = 1,\ 2 \tag{40}$$

In eqn. (40) we can distinguish a contribution of the salt as a whole (first term) and a specific contribution for each ion (second term). The latter is characterized by the electric relaxation time τ_e. Now consider the following three time intervals:

(a) For $t < \tau_e$, $\exp(-t/\tau_e) \sim 1$ and $\exp(-(2k+1)^2 t/\tau_d) \simeq 1$. Therefore,

$$J_i(d/2,\ t) \simeq N'J_0 \left\{ \frac{2D_{3-i} + (-1)^{i-1}D_1 + (-1)^i D_2}{2D_{3-i}} \right\} = N'J_{i0} < j_{i0} \tag{41}$$

$$(N' = N/2) \quad j_{i0} \equiv j(d/\pi L_D)J_{i0} \quad i = 1,\ 2$$

where the definition of J_{i0} given in eqns. (37) has been used.

(b) From $t > \tau_e$ onward (but still $t \ll \tau_d$), we have that $\exp(-t/\tau_e) \to 0$ and $\exp(-(2k+1)^2 t/\tau_d) \lesssim 1$. Then

$$J_i(d/2,\ t) \simeq MJ_0 < j_0 \qquad j_0 \equiv (d/\pi L_D)J_0 \qquad (M < N') \tag{42}$$

Fluxes lose their individual ionic character when t becomes greater than τ_e. M is less than N' because as t increases, the number of terms whose contribution to the sum is not negligible becomes smaller.

(c) For $t \lesssim \tau_d$, close to the limit of validity of hypothesis 3 in Fig. 1, eqn. (40) yields

$$J_i(d/2,\ t) \sim J_0 \tag{43}$$

Since $\exp(-t/\tau_e) \simeq 0$ and the sum of the series is now of the order of its first term, $\exp(-t/\tau_d) \sim 1$.

The steady state concerning matter transport which would be reached for $t > \tau_d$ is well known, both theoretically and experimentally. If $c_L - c_R = \delta c_0$ were to be maintained constant, that steady state would be characterized by a "steady salt flux" J_0. Since this is not the case here, $c_R \to c_L$ as diffusion takes place, and then $J_i \to 0$ (slowly because we have assumed that $l \gg d$). This aspect is not analysed here [22] because our study is focused on the charge separation process ($t \ll \tau_d$) which enables us to maintain the initial assumption of zero fluxes at the interfaces.

Equations (41)–(43) follow from considering the "exact" eqn. (40) for three time intervals. Two interesting phenomena underlying these expressions are (i) the coupling of ionic fluxes so as to give an electroneutral salt flux and (ii) the rising of a flux J_0 for $t \lesssim \tau_d$, because the factor by which the fluxes are multiplied tends to be of the order of unity as $t \to \tau_d$ (this factor has an upper limit, as follows from eqn. 22). Indeed, when $t \to \tau_d$ the number of terms contributing to the series (40) becomes smaller.

(VI.4) Electric current

It is evident that I_q has a non-zero value in the charge separation process studied here, at least locally (over distances of about L_D) and during the "charge-controlled" time domain. Actually, the ELC assumption may be introduced either via "$c_1 = c_2$" or via "$I_q = 0$" (see Appendix 1). Inconsistencies will appear in both cases.

From eqns. (36)–(38) one gets

$$I_q(x, t) = F(J_1 - J_2)$$

$$= I_0 P(x, t)\left\{\left[1 + \frac{2}{\pi}\frac{\delta c_0}{c_0} U(x, t)\right]\exp(-t/\tau_e) - \frac{2}{\pi}\frac{\delta c_0}{c_0} U(x, t)\right\}$$

$$\simeq I_0 P(x, t)\exp(-t/\tau_e)$$

where

$$I_0 \equiv F(J_{10} - J_{20}) = -2F(D_1 - D_2)(c_R - c_L)/d \tag{44}$$

and at the contact point $x = d/2$,

$$I_q(d/2, t) = I_0\left\{\sum_{k=0}^{N'}\exp\left(-(2k+1)^2 t/\tau_d\right)\right\}\exp(-t/\tau_e) \tag{45}$$

Again, the "electric steady state" is characterized by τ_e. Indeed, consider eqn. (45). It readily follows that

$$I_q(d/2, t) = \begin{cases} \simeq N'I_0 \exp(-t/\tau_e) < i_0 \exp(-t/\tau_e) & 0 < t \sim \tau_e \\ \simeq 0 & t > \tau_e \end{cases} \tag{46}$$

where $i_0 \equiv (d/\pi L_D)I_0$. (In eqn. 46 note that, for the first interval, we could assume that $[(2k+1)^2 t/\tau_d + t/\tau_e] \sim t/\tau_e$, since $(2k+1)^2 t/\tau_d \leqslant (2N'+1)^2 t/\tau_d < [(2d/\pi L_D) + 1]^2 t/\tau_d \simeq 4t/\tau_e$. However, for the second interval we have $\exp(-t/\tau_e) \rightarrow 0$.)

The decreasing rate of I_q with respect to t is in agreement with the relaxation equation for $\Delta\phi_t$ obtained previously (eqn. 32): the rising of the potential gradient that slows down the fastest ion and pulls up the slowest one, so that $J_1 = J_2$ ($I_q = 0$), also requires τ_e s.

(VI.5) Estimating the charge carried

The charge carried through the contact plane placed at $x_0 = d/2$ can be estimated below a certain limit:

$$Q_t = \int_0^t I_q(d/2, t)\, dt \simeq N'I_0\tau_e(1 - \exp(-t/\tau_e)) < i_0\tau_e(1 - \exp(-t/\tau_e)) \tag{47}$$

where eqn. (46) has been used. For $t \gg \tau_e$,

$$Q_t(t \gg \tau_e) \equiv Q_0 = N'I_0\tau_e < i_0\tau_e = \frac{2}{\pi}F(D_1 - D_2)\frac{\delta c_0}{L_D}\tau_e \equiv q_0 \tag{48}$$

A previous estimate [2] for Q_0 is $F(D_1 - D_2)(\delta c_0/d)\tau_e$. (Notice that L_D replaces d in q_0 because we have considered the upper limit for the electric current (i_0)

corresponding to the limit beyond which assumption II is no longer valid.) If we were to take $(D_1 - D_2) \sim 10^{-5}$ cm^2/s, $\delta c_0 \sim 10^{-5}$ mol/cm^3, $d \sim 10^{-2}$ cm and $L_D \sim 10^{-7}$ cm, then $Q_0 = (10^{-12} N')$ C $< 10^{-7}$ C $= q_0$.

(VII) DISCUSSION

The transport equations (approximated by Nernst–Planck flux equations) and Poisson's equation have been solved for a given experimental situation outlined in Fig. 1. The charge separation process has been characterized on the basis of the physical magnitudes evaluated in Sections (VI.1)–(VI.5). The relevance of the relaxation times τ_e and τ_d has been clearly shown. The process of electric relaxation that leads to a steady state for the charge transport is represented schematically in Fig. 2.

Equations (41)–(42), (46) and (47)–(48) involve the number of terms N remaining once we have truncated the series by applying assumption (II). We also found in these equations the upper limit that ensures the validity of that assumption. The truncation of the series seems not to be an elegant procedure and might suggest that the representation chosen (eqn. 17) for the time range studied is not completely appropriate. This possibility has to be kept in mind. As a matter of fact, one of the authors who has contributed most to the analytical solution of the equations (MacGillivray, refs. 12 and 18) reported as early as 1970 that "it would seem appropriate to attempt to find analytic solutions valid in the same range $\tau_e \ll t \ll \tau_d$" (we use here our notation) but "of course this may have already been tried and found impossible."

In any case, although admitting the generality of the solution (17)–(20), assumption (II) and the consequences that follow from it seem to have a clear physical meaning. The "effective" thickness of the diffusion zone is not d initially, because the charge separation process occurs over a $\Delta x \sim [(D_1 + D_2)t]^{1/2}$. The characteristic time in our study is τ_e, whence $\Delta x \sim L_D$ (i.e. the thickness d becomes relevant only for $t \sim \tau_d$). Therefore, the concentration gradients giving rise to the initial fluxes of matter and charge develop over distances much shorter than d, and so these fluxes are larger than those observed for $t \sim \tau_d$. This fact is accounted for in our formalism through the N appearing in the series (40). Thus, for $t \leqslant \tau_d$ the "effective" thickness becomes d and the factor N disappears (eqn. 43) for the reasons given in the last paragraph of Section (VI.3). This fact is in agreement with what is observed in the steady state for matter transport.

The upper limit for N is of the order of d/L_D and this is not by chance. Indeed, this parameter shows *how much larger* is the zone over which the concentration and electric potential gradients will be established finally and compares it with the zone in which those gradients are considered "initially". The significance of L_D as a "minimum distance" then becomes clear, because the Debye length indicates the limit of applicability for the macroscopic treatment underlying the equations [1].

The dependence of the "effective" thickness of the diffusion zone of t might suggest considering a transformation of the type $y = x/\sqrt{t}$ for the solution of the
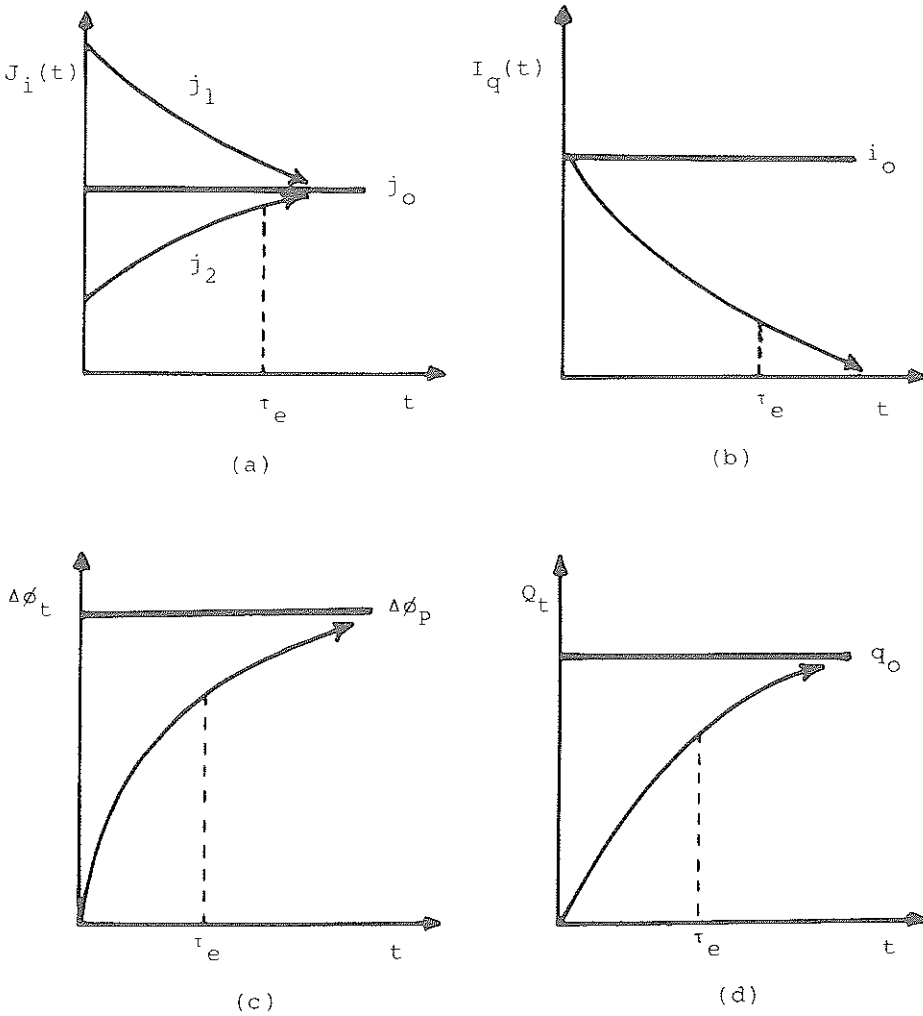
Fig. 2. Schematic representation of the time evolution of the ionic fluxes (a), the conduction current intensity (b), the liquid junction potential (c) and the charge carried (d) during the time interval involved in the charge separation. We assume that $x_0 = d/2$ and that $D_1 > D_2$. The upper limits for J_i, I and Q_t are represented.

problem outlined in Fig. 1. The fact is, however, that this formalism does not lead to a simple analytical solution either, but gives perturbation [19] or numerical [23] solutions.

Equations (40)–(42) can be interpreted as follows. Ions "exist" for $0 < t < \tau_e$ in the sense that ionic fluxes become the flux of the salt for $t > \tau_e$ (i.e. the ionic fluxes lose their identity and give rise to the electroneutral salt flux defined in eqn. 38). As ϵ increases and D_i decreases, τ_e becomes longer: ions behave "independently" for

longer times. This result seems logical since coulombic forces are weaker and ionic diffusion is slower in this case. On the other hand, Leckey and Horne [7] have shown that the liquid junction potential might depend on ionic magnitudes for $t < \tau_e$. Equations (38) support this possibility in the case of the material flux. The above procedure may be considered again, now introducing ionic activity coefficients γ_i [7], and studying the relationship between $J_i(\gamma_i)$ and $J_0(\gamma_{salt})$ during the charge separation process. Of course, this may be a difficult task, especially in the case of multi-ionic systems where the ion–ion interaction is not simple. However, the mathematical part of the problem is accessible, since reliable numerical techniques for its solution are available [3–5,7].

On the other hand, the study of the charge separation process in ion-exchange membranes might provide a basis for a better comprehension of their selective behaviour, especially in those membranes where the matrix-fixed charge exhibits an oscillating behaviour [24]. These topics are open to further investigation.

Still, the enormous experimental difficulties involved in testing the present results should be mentioned as well [7,17]. Even the simple fact of establishing the instant "$t = 0$" is troublesome. Likewise, times of the order of $\tau_e \sim 10^{-9}$ s seem to be beyond any experimental analysis (although some ways of "delaying" the process have been proposed [7]).

In addition to the above-mentioned shortcomings, another difficulty is found: the charge separation process is initiated over regions whose size is of the order of the Debye length [22]. On this scale of distance, the use of macroscopic transport equations is questionable [1–3]. (There would be no problem with the time scale, since the Nernst–Planck equation can be derived from a Langevin formalism for $t > 10^{-13}$–10^{-12} s [1].)

Summarizing, one can safely say that the liquid junction potential reaches its steady-state value "instantly", and the experimentally observable magnitudes, such as the salt flux, for instance, involve times of the order of τ_d or even greater. Indeed, although for $t > \tau_e$, $J_i(d/2, t) \rightarrow J_0$, the salt flux is measured from the change in the volumes on the left of $x = 0$ and on the right of $x = d$ (Fig. 1). These changes take at least $t > \tau_d$.

Despite the above shortcomings, this type of treatment should not be undervalued: it provides a particular *physical model* for describing *how* the charge separation process takes place, and the results arising from it are *consistent* with the experimental observations for "large" times. Of course, the transport of macroscopic quantities of matter (salt) involves times of the order of τ_d and distances of the order of d. But the fact is that the model predicts that charge transport involves times τ_e and distances L_D. Another problem is that 10^{-9} s and 10^{-7} cm are "small" magnitudes for a human to observe [19].

APPENDIX 1: PLANCK'S ANALYSIS

It has been reported previously that Planck's treatment for the liquid junction potential involves ignoring implicitly the charge separation process (i.e. $\tau_e \simeq 0$). In order to show this [2], consider the following dimensionless transformation over the equation for the electric current (2):

$$\left.\begin{array}{l} \bar{x} = x/d \qquad \bar{c}_i = c_i/c_0 \qquad \bar{\phi} = \phi(F/RT) \qquad \bar{D}_i = D_i/(D_1 + D_2) \\ \bar{t} = t\left(\pi^2(D_1 + D_2)/2d^2\right) \qquad \bar{I} = I\left(d/(D_1 + D_2)c_0 F\right) \\ \bar{J}_i = J_i\left(d/(D_1 + D_2)c_0\right) \end{array}\right\} \tag{A1}$$

Thus, one obtains

$$\bar{I} = \sum_{i=1}^{n} z_i \bar{J}_i - (\tau_e/\tau_d)\frac{\partial^2 \bar{\phi}}{\partial \bar{x}\, \partial \bar{t}} \tag{A2}$$

If no electric field is applied externally, $\bar{I} = 0$ (open circuit). If we ignore the time interval involved in the charge separation, $\tau_e \simeq 0$ (actually $(\tau_e/\tau_d) \simeq 0$). By differentiating the resulting equation with respect to $\bar{x}$, one obtains:

$$0 \simeq \sum_{i=1}^{n} z_i \frac{\partial \bar{J}_i}{\partial \bar{x}} = -\sum_{i=1}^{n} z_i \frac{\partial \bar{c}_i}{\partial \bar{t}} = -\frac{\partial}{\partial \bar{t}}\left(\sum_{i=1}^{n} z_i \bar{c}_i\right) \tag{A3}$$

where we have used the continuity equation (3). Now the process studied occurs in an initially ($\bar{t} = 0$) electroneutral system:

$$\sum_{i=1}^{n} z_i \bar{c}_i(\bar{x}, \bar{t} = 0) = 0 \qquad 0 < x < d \tag{A4}$$

Equations (A3) and (A4) lead to

$$\sum_{i=1}^{n} z_i \bar{c}_i(\bar{x}, \bar{t}) = 0 \qquad 0 < x < d \tag{A5}$$

which is the ELC assumption proposed by Planck for the electric charge behaviour along the diffusion zone.

The above approximation seems quite reasonable when $d \gg L_D$, since then

$$\tau_d = (2/\pi^2)\left[d^2/(D_1 + D_2)\right] \gg L_D^2/(D_1 + D_2) = \tau_e \tag{A6}$$

τ_d being the time scale that ensures that the fluxes J_i are constant along the diffusion zone. This last hypothesis, together with ELC, is basic in Planck's analysis. Now when $d \gtrsim L_D$, the processes of "electric" and "diffusional" relaxation nearly overlap; therefore, the potential difference $\Delta\phi_P$ obtained by Planck with $\tau_e \simeq 0$ ($d \gg L_D$) is no longer valid.

From a mathematical point of view, the above fact leads to a revision of assumption II: the liquid junction potential $\Delta\phi_P$ is now the leading term of a series in powers of $(\tau_e/\tau_d) = (L_D/d)^2$. The latter statement has been reported in classical perturbation treatments [12,13,25] and more recently in numerical analyses of the problem [2,14]. Its importance goes beyond the mere inclusion of "correction terms" [13,25] on $\Delta\phi_p$. Indeed, eqn. (27) written in the form

$$\frac{|p_1 - p_2|}{p_i} \sim \left\{\frac{\tau_e}{\tau_d}\right\} \tag{A7}$$

shows that if τ_e and τ_d were comparable, the basic ELC assumption would not be valid. As a matter of fact, according to the excellent work by Guggenheim [21], the "steady state" assumed by Planck would not be reached in the sense that the thickness d is maintained constant artificially, but the liquid junction potential *depends* on d (through the correction terms for $\Delta\phi_P$ containing powers in $(L_D/d)^2$ [25]).

However, as noted before [2], when $\tau_e \sim \tau_d$ ($L_D \sim d$), not only the ELC fails, but also the continuum hypothesis itself, underlying the transport equations and Poisson's equation, becomes questionable.

Finally, it should be mentioned that assuming both bulk solution concentrations to be kept constant artificially, the ELC assumption is not only inconsistent at the very beginning of the charge separation. Once the steady state (for material transport) is reached, let us write ELC in the form $c_1(x) = c_2(x) = c(x)$. By calculating the sums $(J_1/D_1 + J_2/D_2)$ and $(J_1 + J_2)$ from the two Nernst–Planck flux equations, it readily follows that

$$\frac{d^2\phi}{dx^2} = -\frac{RT}{2F}\frac{\alpha(J_1, J_2)}{(D_1 - D_2)c^2}\frac{dc}{dx} \tag{A8}$$

$$\alpha(J_1, J_2) \equiv J_1(D_2/D_1 - 1) + J_2(D_1/D_2 - 1)$$

In order to ensure consistency of ELC with Poisson's equation, the latter should take the form of a Laplace equation, $d^2\phi/dx^2 = 0$. This would be the case if (a) $dc/dx = 0$ and/or (b) $\alpha(J_1, J_2) = 0$. Neither of the two solutions makes sense: (a) is false because $c_L \neq c_R$, and (b) implies that $J_1/J_2 = D_1/D_2$, which amounts to considering $z_1 = z_2$! (Obviously, b would hold provided that $J_1 = J_2 = 0$.) In other words, a steady transport of matter (accompanied by zero net charge transport) requires in our problem a non-zero local net charge density. This fact is well known [10,15,26].

APPENDIX 2: DERIVATION OF EQN. (27)

It is straightforward that $\partial_t p_i \to 0$, as the system approaches the steady state. In this case, eqn. (18) leads to

$$\left|\frac{\partial^2 p_i}{\partial x^2}\right| \sim \frac{|p_1 - p_2|}{L_D^2} \tag{A9}$$

Taking into account that $c_i(x, t) = c_0 + p_i(x, t)$ and $x_0 = d/2$, eqn. (24) yields

$$\frac{\partial^2 p_i}{\partial x^2} = \frac{\delta c_0}{d^2}\left\{-2\pi\sum_{m=1}^{N}\left[m\,\sin\left(\frac{m\pi}{2}\right)\exp\left(-m^2 t/\tau_d\right)\right]\cos\left(\frac{m\pi x}{d}\right)\right\}$$

$$= \frac{\delta c_0}{d^2}\left\{-2\pi\sum_{m=1}^{N}\left[m(-1)^{k+1}\,\delta_{m,2k-1}\exp\left(-am^2\right)\right]\cos\left(\frac{m\pi x}{d}\right)\right\} \quad k\in\mathbb{N}$$

$$\tag{A10}$$

where $\delta_{m,2k-1}$ is the "delta of Kronecker" function, $a \equiv t/\tau_d \leq 1$ and k is a positive, integer number. (Note that the $m - tk$ term of the series is non-zero only when there is a solution to the equation $m = 2k - 1$, $k\in\mathbb{N}$). The series (A10) is an oscillating one and converges rapidly due to the factor $\exp(-am^2)$. Thus keeping in mind that $\delta c_0 \sim p_i$, $|\partial^2 p_i/\partial x^2| \sim p_i/d^2$. Combining this result with eqn. (A9) leads to eqn. (27).

APPENDIX 3: ANALYSIS OF I_q AND I_d

In our treatment, we have maintained the assumption of no externally applied electric fields (open circuit condition). This condition (which amounts to writing $I = 0$ everywhere in the analysis) is already contained in the formulation of the problem: $\partial I/\partial x = 0$ (eqns. 5 and 6) and $I(x = 0, t) = 0 = I(x = d, t)$ (eqn. 11).

According to this, although $I_q \neq 0$ for $t < \tau_e$, even in this time range $I_q + I_d = 0$. In order to verify this, let us consider eqn. (26). One then obtains the following expression for I_d:

$$I_d \equiv -\epsilon\frac{\partial^2\phi}{\partial x\partial t} = \epsilon\frac{2RT}{Fc_0}\frac{c_L - c_R}{d}\frac{D_1 - D_2}{D_1 + D_2}$$

$$\times\left\{\sum_{m=1}^{N}\sin\left(\frac{m\pi x_0}{d}\right)\sin\left(\frac{m\pi x}{d}\right)\exp\left(-m^2 t/\tau_d\right)\right\}$$

$$\times\left\{-\left[\frac{m^2}{\tau_d} + \frac{1}{\tau_e}\right]\exp\left(-t/\tau_e\right) + \frac{m^2}{\tau_d}\right\}$$

$$\tag{A11}$$

where we can introduce the approximation

$$\left\{-\left[\frac{m^2}{\tau_d} + \frac{1}{\tau_e}\right]\exp\left(-t/\tau_e\right) + \frac{m^2}{\tau_d}\right\} \simeq -\frac{\exp\left(-t/\tau_e\right)}{\tau_e}$$

$$\tag{A12}$$

valid for $t < \tau_e$ (see eqn. 46 for I_q). Therefore, using eqn. (44), eqn. (A11) finally yields

$$I_d \simeq -\left(\frac{F^2 c_0(D_1 + D_2)}{\epsilon RT}\right)\epsilon\frac{2RT}{Fc_0}\frac{c_L - c_R}{d}\frac{D_1 - D_2}{D_1 + D_2}P(x, t)\exp\left(-t/\tau_e\right)$$

$$= -I_0 P(x, t)\exp\left(-t/\tau_e\right) = -I_q$$

$$\tag{A13}$$

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