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Electrodiffusion and charge separation

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It has also been realised quite early that there existed some inconsistencies in Planck's theory of diffusion potentials, regarding the electroneutrality principle. Many workers have tried, to account for the inconsistencies, based on charge separation over small intervals of time, distance and the variation of dielectric constant across the junction etc. However, in steady state, these theories adapt themselves, to give Planck's result.

It is proposed to discuss in this paper this problem from the definition of the ionic current and the Nernst-Planck flux equations. This leads to the conclusion that, with the assumptions made by Planck, one can only arrive at the equilibrium potential or the Nernst reversible potential, and cannot get with the given initial and boundary conditions any charge separation even in the nonsteady state.

Key words: Electrodiffusion, charge separation, Planck's theory

Electrodiffusion, the process of diffusion of electrolyte solutions containing ions, is analysed using Nernst-Planck flux equations, giving rise to an expression for the diffusion or liquid junction potential. The earliest of such expressions is due to Planck [1]. However, Planck's solution is shown to have inconsistencies, in that it assumes $C_+(x) = C_-(x)$ and therefore $\rho(x) = 0$; according to Poisson's equation, which is not what the Nersnt-Planck flux equations have.

Later works [2-5] therefore assume $C_+(x) \neq C_-(x)$ and that $\rho(x) \neq 0$. Bass [3] gets the result given below, which incorporates a correction term into Planck's equation.

$$\psi_1 - \psi_0 = \frac{RT}{ZF}\frac{D_+ - D_-}{D_+ + D_-}\left[\frac{C_i(C_1^3 - C_o^3)(C_1 - C_0)^2}{C_o\delta^2 K_o^2 C_o^2 C_1^3}\right] \quad (1)$$

However, if D_+ or $D_- = 0$, the result we expect to get is the Nernst expression which is not what is given by equation (1) above. Thus the above result will be consistent with experimental results only if the correction term is zero, when it becomes identical with Planck's result.

Mafe et al [5] discuss in a series of papers the problems in diffusion potentials. Their results show that in the initial 10^{-9} s, a charge separation process occurs making $C_+(x) \neq C_-(x)$ and $\rho(x) \neq 0$.

However, their results show $C_+(x)$ and $C_-(x)$ would be equal, and more important, independent of x, when $D_+ = D_-$. Since there is no a priori reason as to why D_+ is not equal to D_- we can assume $D_+ = D_-$ to test the result, which gives $C_+(x) = C_-(x) = C_o$ independent of x which is impossible.

According to us, the problem in Planck's derivation lies in the use of the result $I_+ + i_- = 0$. The Nernst-Plancks flux equations imply

$$i_+ = i_{+m} + i_{+d} \quad (2)$$

$$i_- = i_{-m} + i_{-d} \quad (3)$$

$$i = i_m + i_d \quad (4)$$

where $i = (i_+ + i_-), i_m = (i_{+m} + i_{-m}), i_d = (i_{+d} + i_{-d})$

The above equations imply i_+ and i_- are independent and i_m and i_d are independent. The imposition of the condition

$$i_+ + i_- = 0 \quad (5)$$

therefore implies that $i_+ = i_- = 0$ which is the condition for equilibrium. Applying this condition of equilibrium we can see

$$\psi_+ = \frac{RT}{F}\ln\frac{C_1}{C_0}$$

$$\psi_- = -\frac{RT}{F}\ln\frac{C_1}{C_0}$$

and the superposition of potentials results in

$$\psi = \psi_+ + \psi_- = 0$$

which is what is expected under conditions of equilibrium. If an experiment is devised such that the potential between two solutions of same electrolyte with different concentrations are measured using electrodes reversible to either the +ve or -ve ions of the solution under conditions of $i = 0$, we get the Nernst potential.

Symbols

ψ = Electric potential difference
D = Diffusion coefficient
C_1, C_0 = Concentrations of the ions in the two electrolytes
ρ = Charge density
δ = Thickness of the membrane

separating the solutions

K_o^{-1} = is the greatest Debye length in the solution

Other symbols have their usual significance.

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