LETTERS TO THE EDITOR

Shockley-Type Configurations in Ionic Systems: Consequences of Discontinuous Dielectric Constant in Analysis via Poisson-Boltzmann Equation

Dear Sir:

Dr. Bruner's application of the Poisson-Boltzmann equation and the Nernst-Planck phenomenological flux equations to a system containing dissimilar phases raises certain questions which are relevant to both the equilibrium and the steady-state analysis. To help clarify the problems involved which are pertinent to Dr. Bruner's three phase system it is instructive to recapitulate the properties of a case which is relatively more straightforward, namely, a three phase system in which the solvent is *identical* throughout. This immediately circumvents the problem of partitioning of ions, moreover, we have that $K_1 = K_2 = K_3$. Since impermeant species are present in phase 1 and 3 and phase 2 contains only permeant species we have in effect two Donnan systems "back to back."

Recently it has been noted (1) that Shockley's analysis of the semiconductor *p-n* junction at equilibrium constitutes in essence the application of the Poisson-Boltzmann equation to any system containing fixed charges and mobile-charged species. Thus Shockley's analysis via the Poisson-Boltzmann equation applies to an ionic "fixed charge system," e.g. an ion exchange resin in equilibrium with a solution, and to the classical "Donnan equilibrium" in which an ionic species is constrained from moving between the phases by a thin porous mechanical barrier. In fact the Poisson-Boltzmann equation has been applied to the single Donnan system by Bartlett and Kromhout (2) and a numerical computation has been carried out for the electrostatic potential and the concentration profiles of the permeant species, H, Cl, and the impermeant species R^+, as a function of x.

Systems consisting of three phases in series, i.e. two ion exchange resins separated by an electrolytic solution or two Donnan equilibria with a common phase containing only permeant species, constitute the general class of Shockley-type configurations. Systems of this kind can be treated by means of the Poisson-Boltzmann equation (1, 3) to establish potential, field, and concentration profiles as a continuous function of x. Turning to the steady state of current flow, if the fixed charge is of the same sign in phases I and III the asymmetrical I, ψ behavior vanishes as the thickness of phase II approaches zero. However, if the fixed charges are of opposite sign then we have in general a "*p-i-n*" configuration and, in this case, as the thickness of phase II approaches zero the abrupt transition gives rise to the "*p-n* junction" with marked rectification maintained (4).

In sharp contrast a formidable problem arises if the phases are dissimilar. In general, in addition to the electrostatic potential barrier, energy barriers are present owing to ions interacting with the medium constituting the given phase. Thus two empirical facts are observed with respect to a given ionic species, namely, partitioning occurs between two phases such that the phase with the higher dielectric constant contains a given ion at the higher concentration and vanishingly small but finite difference can occur in the concentration of positive and negative species. The former condition is revealed by direct chemical analysis and is usually given as the "partition coefficient." The latter condition, on the other hand, cannot be measured directly but may be measured with some ambiguity by electrometric techniques and is known as "the phase-boundary potential." Leaving aside the ambiguity in the magnitude of this potential which has concerned many investigators and even compelled some theoreticians to consider this potential as inadmissible (5), an electrical state can arise which is associated with the sharp discontinuity in concentration of the mobile species and the space charge due to asymmetry in the positive and negative ions. The partitioning effect thus *must* be taken into account for a complete and physically meaningful solution of the Poisson-Boltzmann equation throughout the region of the membrane phase. This analysis has been carried out by Verwey and Niessen for the equilibrium state (1966. *Biophys. J.* **6**:371).

For those investigators who are studying the electrical properties of Rudin and Mueller films (phospholipid-hydrocarbon films) similar considerations are particularly relevant.

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The Electrical Conductance of Semipermeable Membranes

Dear Sir:

I had the privilege of reading the two papers of Dr. Bruner on the electrical conductance of semipermeable membranes (1965. *Biophys J.* **5**:867, 887). In addition, I had the opportunity to study the preprint of Dr. Bruner's third paper of this series and reflect on Dr. Mauro's comments regarding the assumptions invoked in these papers (1966. *Biophys. J.* **6**:367). Basically, Dr. Bruner's development begins with the combination of Poisson's equation with classical equation for ion current density. Since subsequent developments in his procedure have led to differences of opinions about the validity of some of the author's assumptions, it may be appropriate to point out certain relevant difficulties that one has to overcome in theoretical development of this kind. In my opinion, only then, we will be able to resolve satisfactorily these differences of opinions.

The recognition of discontinuity in dielectric constant at the interface compels one to include (and not discard) the image potential terms and corrections to local activity coefficients (see Buff and Stillinger. 1963. *J. Chem. Phys.* **39**:1411) to the classical equations, in the determination of concentration profiles in inhomogeneous boundary regions. Our understanding of equilibrium state of such inhomogeneous fluid regions is far from complete and one should appreciate the efforts of Levine, Bell (1960. *J. Phys. Chem.* **64**:1188), and Loeb (1951. *J. Colloid Sci.* **6**:75), before introducing assumptions regarding the continuous or dis-