

# Electrochemistry, Well Posed

Bob Eisenberg  
Department of Molecular Biophysics and Physiology  
Rush University  
Chicago IL 60612  
USA

February 17, 2012

The work reported here was stimulated by intensive discussions with Chun Liu, Pennsylvania State University, and would not have occurred without them. The particular formulation of the Poisson Nernst Planck system I use here is that being used in work in collaboration with Allen Tzyy-Leng Horng, Feng Chia University, Taichung, Taiwan, Tai-Chia Lin 林太家 of the National Taiwan University Taipei, and Chun.

Biology and chemistry occur in ionic solutions for the most part. Water without ions is lethal for cells and most proteins. Chemistry is often done in ionic solutions. Little more needs to be said about the significance of ionic solutions beyond references XXXXX.

Ions in water like  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cl}^-$  move approximately as hard spheres in a resistive dielectric as described by the implicit solvent (so-called) primitive (or implicit solvent) model of electrolyte solutions. A good representation of this primitive model is given by the Poisson Nernst Planck equations once it is modified to deal with finite size ions.

Partial differential equations of this sort couple diffusion, migration, and the electric field and form a system that must be mathematically well defined if they are to be solved. The formulation of a well posed version of these equations, starting at time zero, progressing to time infinity, including multiple species is addressed here. I am unaware of previous treatments of this problem that produce well posed mathematical problems for all mixtures of ions on this complete time scale, although such treatments may well exist beyond the horizon, of my knowledge and experience.

The fundamental difficulty is that the equations have usually been viewed as typical flow, conservation of mass, etc. equations, in the tradition of the fluid mechanics of (mostly uncharged) systems. But the ions flowing are charged, the experiments are designed to deal with electrical current and potential first, and the flux of the ions is not dealt with directly in most experiments. The flux of electrical charge (i.e., the electrical current density) is NOT AT ALL the same as the flux of ions or the flux of mass. It is my contention that the equations of PNP must be written and solved so that the electrical properties are dealt with first, and as accurately as possible, and residual difficulties, if any, appear in the flux and concentration of the least important ions. Because electrical forces and flows are on a different scale from diffusion forces and flows, this can make a very large difference numerically. Electrical forces and flows are very large, and act on a very fast time scale (sometimes faster than microseconds). Indeed, on short enough time scales, the difference in concentrations of positive and negative ions that is well within the roundoff error of even double precision computer arithmetic can dominate the problem creating dreadful artifacts. That is one of the issues we deal with here. Diffusion forces and flows are very much weaker and act typically on a time scale of minutes or longer. Of course, integrated to time infinity, the diffusion forces and flows can produce concentration changes of great (even unlimited) importance. That is another of the issues we deal with here. It is precisely that issue we deal with here. Finally, the actual setups used to record currents have limited ability to record things faster than say 10 microseconds mostly because of 'stray capacitances' (i.e., displacement currents from one place to another). I believe numerical problems will be much easier if this NATURAL and UNAVOIDABLE property of the real world is included in the formulation of the PNP model and its numerical solution. I might be wrong, of course, being intensely (and proudly) human, and (not so proudly) prone to error.

The equations we consider are just the PNP equations themselves, with ions treated as points, since as far as I can tell the issues of well posedness are the same as in more realistic models like the primitive model mentioned above.

The central issue is that **boundary conditions are always set using electrical variables**, electrical potential and electrical current. But the PNP equations as usually written specify the flux of ions, not the flux of electrical charge. The current is the sum of the (weighted) fluxes of the PNP equation, plus the capacity current. The numerical implementation of PNP done this way is always on the edge of disaster. It is very very easy somewhere to try to estimate NET charge (the variable on the right hand side of Poisson), or flux of current, or charge on the boundary etc by subtracting the concentrations, flux of ions, or concentrations on the boundary. Any attempt to estimate electrical variables by subtracting ‘chemical’ variables is likely to produce disaster. We shall see that more is involved than simple algebra. There is a tension then between the obvious and usual formulation and boundary conditions for PNP, which specify all of the fluxes, and not the current, and the electrical boundary conditions actually used and needed. There is also additional physics usually left out of formulations of PNP that is needed to make the system well posed (1) at zero time and(2) at infinite time, and (3) to make time scales easily computable, in my opinion. Statement (3) has not been proven and is subject to debate in my view.

The solution to these problems proposed here is meant to replicate the laboratory situation. it includes a ‘shunt’ pathway for flux of ions and a separate shunt pathway for current flow (through a capacitor which conducts ELECTRICAL CURRENT INDEPENDENT OF THE IONIC NATURE OF THE CHARGE that carries current) in addition to boundary conditions for the potential, and all but one of the concentrations. The shunt pathway for flux is chosen so it only conducts the neglected flux (the one left out of the set called “all but one”) and conducts it with a flux very much less than the peak flux of that ion during experiments.

Now, to equations.

Here is a version of PNP in which Maxwell’s version of the continuity equation **for charge**<sup>1</sup> is used so the resulting flux equation for the flux **J** of charge (i.e., flux of total electric current) always involves the permittivity (i.e., dielectric coefficient).

$$\begin{aligned}\nabla \cdot \mathbf{J} + \frac{\partial \rho}{\partial t} &= \nabla \cdot \left( \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \right) = 0; \\ \nabla \cdot \mathbf{J} + \frac{\partial \rho}{\partial t} &= \nabla \cdot \left( \mathbf{J} + \frac{\partial (\varepsilon \mathbf{E})}{\partial t} \right) = 0\end{aligned}\tag{1}$$

This is eq. 6.4 of Jackson, p. 238, expanded, see p. 154. I follow Jackson’s notation exactly and use  $\varepsilon$  for the permittivity (that has units. It is not the dielectric ‘constant’).

The variable  $\rho$  is the net charge, related to the concentration of ions through

$$\rho = \sum_{i=1}^N z_i F c_i\tag{2}$$

where we use chemical units (Faradays) because we are dealing with a macroscopic system.

<sup>1</sup> See p. 238 of J. D. Jackson, *Classical Electrodynamics*, Third Edition (1999), attached to this document.

Now we introduce the Nernst Planck equations for the flux of individual ions (NOT the flux of ionic current, rather the flux of the number of ions). Remember ions of different valence  $z_i$  are very important in biology (calcium ions have charge +2; chloride ions have charge -1; sodium and potassium ions have charge +1). They all have significantly different diffusion coefficients. It is NEVER permissible to treat all ions as having the same diffusion coefficient or the same (magnitude let alone sign) of charge if one wants to deal with biology.

$$\mathbf{J}_i = -D_i \left( \nabla c_i - \frac{F}{RT} z_i c_i \nabla \phi \right); \quad i = 1, \dots, N \quad (3)$$

I use the diffusion coefficient and not mobility to avoid the confusion between the two definitions of mobility (absolute and electrical) in the literature. Obviously if the Einstein approximation fails and enough information is available to distinguish mobility from diffusion coefficient, the mobility should be used explicitly, and the choice of definition should be made explicitly.

Now, we sum over all the ions to get total flux of charge

$$\mathbf{J} = \sum_{i=1}^N \mathbf{J}_i = \sum_{i=1}^N \left( -D_i \nabla c_i - \frac{F}{RT} z_i c_i \nabla \phi \right) \quad (4)$$

Maxwell Continuity eq. (1) gives the equation for continuity of electric charge, i.e., current

$$\nabla \cdot \mathbf{J} = \nabla \cdot \left[ \sum_{i=1}^N \left( -D_i \nabla c_i - \frac{F}{RT} z_i c_i \nabla \phi \right) \right] = -\nabla \cdot \left( \frac{\partial(\epsilon \mathbf{E})}{\partial t} \right) = -\nabla \cdot \left( \frac{\partial(\epsilon \nabla \phi)}{\partial t} \right) = \frac{\partial(\epsilon \nabla^2 \phi)}{\partial t} \quad (5)$$

I leave the permittivity inside the brackets so we never forget the assumption that is involved in moving it outside! And then the classical continuity equation for the flux of charge  $\mathbf{J}$  (remember  $\mathbf{J}$  is the flux of charge, not the flux of ions).

$$\nabla \cdot \mathbf{J} = \nabla \cdot \left[ \sum_{i=1}^N \left( -D_i \nabla c_i - \frac{F}{RT} z_i c_i \nabla \phi \right) \right] = -\frac{\partial \rho}{\partial t} \quad (6)$$

$$\nabla \cdot \mathbf{J} = \sum_{i=1}^N z_i F \frac{\partial c_i}{\partial t} \quad (7)$$

It is very important that no attempt be made to compute the sum on the right hand side of eq. (7) from the concentrations  $c_i$ . The sum  $\sum_{i=1}^N z_i F \frac{\partial c_i}{\partial t}$  is ill posed. Rather, one must compute  $\rho$  the net charge and its time derivative directly without summing concentrations or their rate of change.

Note the different form of the continuity of mass for each species

$$\nabla \cdot \mathbf{J}_i + \frac{\partial c_i}{\partial t} = 0 \quad (8)$$

and the different form for the continuity equation of total 'mass'.

$$\sum_{i=1}^N (\nabla \cdot \mathbf{J}_i) = -\sum_{i=1}^N \frac{\partial c_i}{\partial t} = -\frac{\partial}{\partial t} \sum_{i=1}^N c_i \quad (9)$$

The mass continuity equations are **not** equivalent to the Maxwell continuity equation. They do not involve the charge  $z_i F$ , at all. For example, the sum  $\frac{\partial}{\partial t} \sum_{i=1}^N c_i$  is well posed and easy to compute because all its terms are positive while the corresponding terms in the sum in eq. (7) can be positive or negative, and must be nearly equal, because of the enormous strength of electrical forces, summarized by the (approximate) physical principle of electroneutrality. In order to avoid confusion we do not even have a symbol for the flux of total mass  $\sum_{i=1}^N \mathbf{J}_i$ .

**Boundary Conditions.** We now have difficulty when we set boundary conditions. We need to set boundary conditions on the electrical current  $\mathbf{J}$  but the usual formulation of PNP sets boundary conditions on all  $N$  of the ionic species. This obviously over-specifies the problem.

This apparent paradoxical situation is resolved when we realize that to make the system well posed (i.e., to reach steady state when concentrations and potentials on the boundaries are constants independent of time), we must **relax our boundary conditions on concentration. We must allow one of the concentrations  $c_m$  (say) to 'float', i.e., to be determined by the rest of the problem.**

We introduce an artificial additional pathway for this ion we call the leak pathway, e.g., an  $(N+1)^{th}$  flux equation added to the set described in eq. (3).

We now have two flux equations for the same ionic species, one the real one and the other the leak. We choose parameters for the leak so the system is not perturbed in the time domain we study. The leak ensures that at infinite time the system will be stable.

**Set Of Equations Including Leak Conductance** are then

- (1) The Maxwell Continuity Equation for the total flux of charge

$$\nabla \cdot \mathbf{J} = \nabla \cdot \left[ \sum_{i=1}^N \left( -D_i \nabla c_i - \frac{F}{RT} z_i c_i \nabla \phi \right) \right] = \rho \quad (10)$$

- (2) The mass continuity equations for the (mass) flux of  $N - 1$  species. This set excludes ion  $m$ :

$$\mathbf{J}_i = -D_i \left( \nabla c_i - \frac{F}{RT} z_i c_i \nabla \phi \right); \quad i = 1, \dots, N - 1; \quad \text{ion } m \text{ is excluded} \quad (11)$$

- (3) Dirichlet boundary conditions on the concentrations of  $N - 1$  species, ion is excluded, imposed at time zero, and maintained from then on.

- (4) Some initial condition on ion  $m$  which is not maintained in time so the system starts in a well-defined state close to electrical neutrality. We will discuss what 'close to electrical neutrality' means next.

- (5) We need to choose parameters for the leak ion  $m$ . Choose the numerical value of the leak "conductance" so it has no effect on the system in the times we are interested in. (This will depend on the size of the baths etc). A looser way to choose it is to make the leak conductance 0.001 times the conductance of the rest of the system. The leak conductor guarantees that flux build up is handled correctly.

NOTE THAT WITHOUT THESE PROCEDURES EXPERIMENTS. CANNOT BE DONE. So it is not surprising that they are needed in theory. NOTE that the amazing thing is that people like me have taken so long to realize we need to specify all this to theoreticians.