**Electrochemistry, Well Posed**

Bob Eisenberg

Department of Molecular Biophysics and Physiology

Rush University

Chicago IL 60612

USA

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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 Na+, K+ and Cl− move approximately as hard spheres in a frictional 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 round-off 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**, usually electrical potential and measurements are usually made of electrical current. But the PNP equations as nearly always written to 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 replicatethe 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***[[1]](#footnote-1) is used so the resulting flux equation for the flux  of charge (i.e., flux of total electric current) always involves the permittivity  (i.e., dimensionless dielectric coefficient × permittivity of free space). Everything starts with Poisson



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



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

These equations hide a crucial numerical fact. In bulk solutions and many other places and conditions  is very very close to zero, with  The enormous strength of the electric field forces the net charge to be very small. If the net charge is not small, large gradients of potential exist which destroy biological systems. As a rule of thumb, membranes, proteins and ion channels are destroyed if potentials of 200 mV are applied to a system or fields are larger than 200 mV/(thickness of a lipid membrane = 2 nM)= 2x106 volts/cm. When  is this small, it cannot be computed by executing the sum shown in eq.. Indeed, eq. can be used to determine a particular concentration  from the other concentrations, if for some reason  is not known, but it can never be used to determine . Round off and other errors make eq. useless for computation. Rather, the Poisson equation itself must be used to compute .

The flow equation for the total charge are



or if we suppress Maxwell’s dreadful displacement field  (introduced before the electron was discovered and so before permanent charge was known to exist) and use more modern notation



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

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).



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.

It is important to remember that ions of different charge (i.e., valence) *zi* are very important in biology (calcium ions Ca2+ have charge +2; chloride Cl− ions have charge −1; sodium Na+ and potassium K+ 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.

Next, we relate eq. and by explicitly summing over all the ions to get total flux of charge



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



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





It is very important that no attempt be made to compute the sum on the right hand sides of eq.  from the concentrations . The sum  is ill posed, and must be nearly equal to zero, because of the enormous strength of electrical forces, summarized by the (approximate) physical principle of electroneutrality. One must never compute the sum . Rather, one must compute  the net charge and its time derivative directly, for example, from the Poisson equation , without summing concentrations or even their rate of change. In fact, the numerical properties of  are so different, depending on how it is computed, that it would be wise to use separate symbols in computer programs for the  of eq. and the  of eq. , on the right hand side of the Poisson equation.

Note the form of the continuity of mass for each species



and the form for the continuity equation of total ‘mass’.



The mass continuity equations are ***not*** equivalent to the Maxwell continuity equation. They do not involve the charge  at all For example, the sum  is well posed and easy to compute because all its terms are positive while the corresponding terms in the sum for net charge  in eq.  can be positive or negative. In order to avoid confusion we do not even have a symbol for the flux of total mass .

**Boundary Conditions**. We need to set boundary conditions on the electrical potential and charge, and write equations defining how we measure current  to correspond with experiment. But the usual formulation of PNP sets boundary conditions on all *N* of the ionic species and ignores the experimental reality that  is measured, not  It is obviously impossible to specify *N* concentrations and deal with their fluxes as if they are independent, and also place conditions on the total current 

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  (say) to ‘float’, i.e., to be determined by the rest of the problem. We also must allow the charge  to float, to be determined by the rest of the system. We do this by including additional pathways for flux and current. These additional pathways always exist in experiments. The pathway for electrical current is the shunt capacitance Cshunt . The pathway for individual ionic flux current is the leak or shunt capacitance Cshunt .*** This pathway can be described by an  flux equation in addition to the set of *N* equations described in eq. .

We now have two flux equations for the same ionic species, one the real one and the other the leak. This does not cause trouble in the cases of interest because we can choose parameters for the leak path so the system is not perturbed in the time domain we study. The leak ensures that at infinite time the system will be stable, just as ther shunt capacitance ensures that when voltage is changing rapidly, the system behaves reasonably, e.g., at short times.

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

1. The Maxwell Continuity Equation for the total flux of charge



1. The mass continuity equations for the (mass) flux of  species. This set excludes ion *m*:

 ion *m* is excluded

1. Dirichlet boundary conditions on the concentrations of  species, ion is excluded, imposed at time zero, and maintained from then on.
2. 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.
3. 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 the properties of the leak is to choose parameters so the leak flux is 0.001 times the flux of the rest of the system. Typical values in experiments would be 100 gigohms, i.e., 10 pico siemens in electrical units. The leak path guarantees that flux build up is handled correctly.

Note that without these leak paths 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.

Next, we discuss why we need the shunt capacitance. The reason is that as we specify the concentrations at time  we cannot choose them well enough to guarantee that  Numerical errors of one sort or another will produce a  that has large effects that can embarrass our calculation. The way to deal with this is the way it happens in real life. The shunt capacitance provides a path by which this charge can quickly flow and equilibrate. Typical values are 50 – 100 pF.

1. See p. 238 of J. D. Jackson, *Classical Electrodynamics*, Third Edition (1999), attached to this document. [↑](#footnote-ref-1)