A new open source software for the calculation of the liquid junction potential between two solutions according to the stationary Nernst–Planck equation

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May 17, 2014

Abstract

We describe an open source software which we have realized and made publicly available at the website [http://jljp.sourceforge.net](http://jljp.sourceforge.net). It provides the potential difference and the ion fluxes across a liquid junction between the solutions of two arbitrary electrolytes. The calculation is made by solving the Nernst–Planck equations for the stationary state in conditions of local electrical quasi-neutrality at all points of the junction. The user can arbitrarily assign the concentrations of the ions in the two solutions, and also specify the analytical dependence of the diffusion coefficient of each ion on its concentration.

1 Purpose and description of the software

A liquid junction potential develops when two solutions containing ions of different species and/or concentrations come into contact [1]. Although it may affect in a significant way several types of electrochemical measurements, it is very difficult to measure directly in a given experimental setup. Hence a proper correction of the results for the presence of liquid junction potentials requires a tool for their theoretical calculation. Commercial programs exist, specifically designed for biomedical applications [2], with which such a calculation can be performed, but to our knowledge until now there existed no open source software freely available to the scientific community, and easy to use in the most general situations. The program we are presenting in this paper is written in Java and is available as an applet, with a simple and user-friendly graphical panel, at the site [http://jljp.sourceforge.net](http://jljp.sourceforge.net). In order for the program to be run via a web browser, the Java plugin must have been installed. We point out that the standard security settings on MS Windows operating systems may prevent the operation of the program. This problem can be however easily solved by suitably modifying the Java security options through the Windows Control...
Panel. The free download of the package or of the source files from the site sourceforge.net is also possible.

The program accepts as an input the ion concentrations at the boundaries of the junctions. The number $n$ of ion species that one can consider is free. For each of them one has to assign the electrical charge and the mobility. The former is a multiple of the elementary charge $e$, and is therefore expressed as a relative integer $z$. The latter is defined in general as the ratio $\mu = v/F$ between a drift velocity and the applied force which generates the drift, and is therefore expressed in units $\text{m s}^{-1} \text{N}^{-1}$. For all the most common ions these parameters are automatically provided by the software as soon as the ion’s name is entered in the graphical panel. In general it is however also possible to introduce the values by hand. The final output is represented by the junction potential $V$ and by the ionic fluxes, i.e. the number of ions of each species that flow through each section of the junction per unit time.

The calculations are performed by numerically integrating the stationary Nernst–Planck equations \cite{3,1} in conditions of assumed local electrical quasi-neutrality at all points of the junction. This represents an additional advantage with respect to the available commercial software, which makes instead use of the less accurate Henderson’s equation \cite{4,1}. Furthermore, our program also gives the possibility to deal with nonideal junctions, i.e. with junctions in which the activity of the ions cannot be identified with the concentration. This is normally the case whenever the concentrations are not so low. Denoting with an index $i$ the ion species present in the junction, $1 \leq i \leq n$, it is possible to specify in an almost arbitrary way the functional dependence of the activity $a_i$ of an ion on its concentration $c_i$, assuming that the dependence on the concentrations of the other ions can be neglected. This is done by giving as an input the analytical form of the function $d \ln a_i/d \ln c_i$, which is used in the calculation of the junction potential as explained below.

2 Theory

The Nernst–Planck equation describes the concentration profile of an ion which moves inside the liquid junction under the influence of diffusion and of the electric field. In a stationary regime and in the absence of chemical reactions, owing to the continuity equation the flux $\Phi_i$ of the ion is constant along the junction. If $L$ is the length of the junction and $x$ the spatial coordinate, with $0 \leq x \leq L$, the Nernst–Planck equation for the $x$-dependent concentration $c_i$ is

$$\Phi_i = -D_i \frac{dc_i}{dx} + z_i \mu_i c_i eE$$

(1)

where $D_i$ is the diffusion coefficient of the ion, while $e$, $z_i$ and $\mu_i$ are defined as above. If we suppose that the condition of electrical neutrality

$$\sum_{i=1}^{n} z_i c_i = 0$$

(2)
is satisfied at all points of the junction, then using (11) it is possible to express
the electric field as
\[ E = \frac{A}{e \sum_{j=1}^{n} c_j z_j^2 \mu_j / D_j} \]  
(3)
where \( A = \sum_{k=1}^{n} z_k \Phi_k / D_k \). Taking into account that, as a consequence of
(2), the concentration \( c_n \) of the last ion can be expressed as a function of the
others as \( c_n = - \sum_{i=1}^{n-1} c_i z_i / z_n \), one finally obtains a system of \( n - 1 \) differential
equations in the unknowns \( c_1, \ldots, c_{n-1} \):
\[
\frac{dc_i}{dx} = \frac{1}{D_i} \left( -\Phi_i + ez_i \mu_i c_i E \right)
= \frac{1}{D_i} \left( -\Phi_i + \frac{z_i \mu_i c_i A}{\sum_{j=1}^{n-1} \left( z_j \mu_j / D_j - z_n \mu_n / D_n \right) c_j z_j} \right)
\]  
(4)
In the hypothesis mentioned above, that the activity \( a_i \) depends only on \( c_i \),
the diffusion coefficients can be expressed as
\[ D_i = kT \mu_i \frac{d \ln a_i}{d \ln c_i} \]  
(5)
where \( k \) is Boltzmann constant and \( T \) the absolute temperature. The program
calculates \( D_i \) as a function of \( c_i \), by using in the right-hand side of the above
equation the analytical expression provided by the user. By default, the program
assumes that the ideal relationship \( a_i = c_i \) holds. Note that in such a case, the
well-known Einstein’s relation \( D_i = kT \mu_i \) is obtained.
After the user has entered the values \( c_1^A, c_2^A, \ldots, c_{n-1}^A \), \( c_1^B, c_2^B, \ldots, c_{n-1}^B \), of
the ion concentrations at the two sides A and B of the junction (\( c_n^A \) and \( c_n^B \)
being fixed by the condition of electrical neutrality), the program integrates
the differential equations (4) for an initial guess of the parameters \( \Phi_1, \ldots, \Phi_n \),
taking the concentrations on side A as initial data. Since it is assumed that
the total electrical current through the junction vanishes, these parameters are
subject to the condition
\[ \sum_{i=1}^{n} z_i \Phi_i = 0 \]
As independent variable for the integration, the concentration \( c_1 \) of the first ion
is taken in place of the coordinate \( x \), which does not appear on the right side of
(4). The procedure is automatically iterated for suitably modified values of
the fluxes \( \Phi_i \), until the concentration \( c_2, \ldots, c_{n-2} \) for \( c_1 = c_1^B \) are close to the
assigned values \( c_2^B, \ldots, c_{n-2}^B \) within an acceptable tolerance. Then, by using the
equations (4) again, \( x \) is in turn calculated as a function of \( c_1 \). In this way the
program obtains a value for the length \( L \) of the junction and for the potential
\[
V = V_B - V_A = -\int_0^L E \, dx = \int_{c_1^A}^{c_1^B} \frac{AD_1 dc_1}{e \Phi_1 \sum_{j=1}^{n} c_j z_j^2 \mu_j / D_j - ez_1 \mu_1 c_1 A}
\]  
3
The value of $L$ obtained in this way has actually no physical meaning. The fluxes $\Phi_1, \ldots, \Phi_n$, for which the boundary conditions on side B are satisfied, are in fact not univocally determined: their multiplication by an arbitrary numerical factor $\lambda$ does not change either the concentrations or the junction potential, but only amounts to dividing by $\lambda$ the length $L$ of the junction. It follows that only the values of $L\Phi_1, \ldots, L\Phi_n$, which are provided as the program’s output together with $V$, are independent of the arbitrary factor $\lambda$, and indeed represent the ion fluxes multiplied by the length of the junction. The actual length $L$ of the physical junction does not affect the value of the potential, and is not required as an input by the program.

In principle the results should be independent of the choice of the ion whose concentration is taken as independent variable. The user can verify this by repeating the calculations with different choices, and then comparing the results. It is obvious that, in order to suitably play the role of independent variable, the concentration of an ion must be a monotonic function of the position. To verify that this condition is fulfilled, it is possible to inspect the concentration profiles along the junction, which can be also obtained as outputs from the program.

3 An example

We have applied our program to the case in which a solution 0.1 M of zinc chloride $\text{ZnCl}_2$ is present on side B of the junction, while on side A there is a solution 0.1 M containing a mixture of potassium acetate KOAc and potassium chloride KCl. If we call $\alpha$ the fraction of acetate with respect to the total solute on side A of the junction, for $\alpha = 0$ we have only KCl, while for $\alpha = 1$ we have only KOAc. The junction is supposed to be ideal. In Fig. 1 we report, as a function of $\alpha$, the liquid junction potential calculated either with our numerical software based on the Nernst–Planck equation, or according to the Henderson formula. For $\alpha$ approaching 0 the numerical result converges to the value $V_0 = 12.7 \text{ mV}$, which can also be obtained by analytical methods [5], since for $\alpha = 0$ only three ion species are present in the junction. The accordance with exact analytical solutions of the Nernst–Planck equations has also been verified for junctions with only two ionic species. These facts confirm the correctness of the numerical program. We see on the other hand that, for all values of $\alpha$, the junction potential is somewhat underestimated by the Henderson formula.

References

[1] D. MacInnes, *The Principles of Electrochemistry*, Dover, New York, 1961.

[2] P. H. Barry, Journal of Neuroscience Methods 51, 107 (1994).

[3] M. Planck, Ann. Phys. Chem. 39, 161; 40, 561 (1890).

[4] P. Henderson, Z. physik. Chem. 59, 118 (1907); 63, 325 (1908).
Figure 1: Liquid junction potential between a solution 0.1 M of a mixture of KOAc and KCl on one side, and a solution 0.1 M of ZnCl$_2$ on the other. The abscissa $\alpha$ is the fraction of acetate on the first side.

[5] M. Marino, L. Misuri, A. Carati and D. Brogioli, unpublished.