Nernst-Planck equation

The main problem of the previous approaches is that it is very difficult to estimate the coupling between ionic fluxes. In the Nernst-Planck approximation it is assumed that

$$\ell_{i,k} = 0 \quad ; \quad i \neq k \tag{3.1}$$

This seems to mean that the fluxes are decoupled but due to the electroneutrality condition and the definition of electric current density,

$$\vec{I} = F \sum_i z_i \vec{j}_i \tag{2.24}$$

there is strong coupling. Hence, writing the ionic phenomenological equation and expanding the electrochemical potential,

$$\vec{j}_i = -\ell_{i,i} \nabla \tilde{\mu}_i = -\ell_{i,i} \left(RT \nabla \ln c_i + z_i F \nabla \phi \right) \tag{3.2}$$

and introducing the phenomenological coefficient

$$\ell_{i,k} = \frac{D_i c_i}{RT} \tag{3.3}$$

we reach the **Nernst-Planck equation**:

$$\vec{j}_i = -D_i \left(\nabla c_i + z_i f c_i \nabla \phi \right) \quad ; \quad f = F / RT \tag{3.4}$$

Above equation applies in the Hittorf reference frame or, in the absence of convection, in the fixed laboratory coordinates.

If there is convection in the system (e.g. solution flow across a membrane), we add the corresponding term:

$$\vec{j}_i = \underbrace{-D_i \nabla c_i}_{\text{diffusion}} \quad \underbrace{-\; z_i f c_i D_i \nabla \phi}_{\text{migration}} \quad \underbrace{+\; \vec{v} c_i}_{\text{convection}} \quad \left(= \vec{j}_i^{\,H} + \vec{v} c_i \approx \vec{j}_i^{\,m} + \vec{v} c_i \right) \tag{3.5}$$

Ionic flux thus depends on three factors: diffusion due to the concentration gradient (Fick's law), migration (electrophoresis) due to the potential gradient and convection due to the solvent flow (pumping, stirring). It has to be realized that the convection term does not originate from the gradient of the electrochemical potential but due to mechanical forces. It merely makes the connection between the reference frames. Solvent flow due to the gradient of the chemical potential of the solvent – i.e. osmosis – is possible but that requires an osmotic membrane that does not (in principle) allow any solute flow.

Let's multiply Eq. (3.5) by z_i and sum over all the species:

$$\sum_i z_i \vec{j} = \frac{\vec{I}}{F} = -\sum_i D_i z_i \nabla c_i - f \nabla \phi \sum_i z_i^2 c_i D_i + \vec{v} \sum_i z_i c_i \tag{3.6}$$

The first observation is that the last term is zero due to electroneutrality, i.e. convection has no contribution to electric current. Solving $\nabla \phi$ from above, it is obtained

$$-\nabla \phi = \frac{\vec{I}}{\left(F^2 / RT\right) \sum_i z_i^2 c_i D_i} + \frac{RT}{F} \frac{\sum_i z_i D_i \nabla c_i}{\sum_i z_i^2 c_i D_i} = \frac{\vec{I}}{\kappa} + \frac{RT}{F} \frac{\sum_i z_i D_i c_i \nabla \ln c_i}{\sum_i z_i^2 c_i D_i} = \frac{\vec{I}}{\kappa} + \frac{RT}{F} \sum_i \left(\frac{t_i}{z_i} \right) \nabla \ln c_i = \boxed{\frac{\vec{I}}{\kappa} + \frac{1}{F} \sum_i \left(\frac{t_i}{z_i} \right) \nabla \mu_i} \tag{3.7}$$

In Eq. (3.7) we have used the conductivity of the solution

$$\kappa = \frac{F^2}{RT}\sum_i z_i^2 c_i D_i \tag{3.8}$$

and the transport number of an ion *i*:

$$t_i = \frac{z_i^2 c_i D_i}{\sum_k z_k^2 c_k D_k} = \frac{\kappa_i}{\kappa} \tag{3.9}$$

Eq. (3.7) has a very deep message. Potential drop in the system has an irreversible contribution, **ohmic loss**, $-\vec{I}/\kappa$, and a reversible part, **diffusion potential**. In the absence of concentration gradients, we can write the Ohm's law $\vec{I} = \kappa\vec{E}$ and the dissipation function $\theta_{\text{ohm}} = \vec{I}\cdot\vec{E} = \kappa E^2 = I^2/\kappa$ that is known as **Joule heat**. Although electric current were zero, ionic fluxes exist due to diffusion potential, but the fluxes of cationic and anionic species must balance each other so that electro-neutrality is maintained. Ohmic potential drop always comes from an external source and diffusion potential is an internal property, arising from the differences between the ionic mobilities (see eq. (2.88) in the textbook). Therefore, diffusion potential usually is rather low, unless a system includes ions with significantly high mobility, such as H^+ or OH^-, or very large ions with low mobility.

As explained in detail on p. 54 of the textbook, the difference between ionic migration and conduction is that the former takes place due to the total potential gradient, including both the ohmic and diffusion potential, while the latter comes only from the external source (current). When we carry out an electrochemical experiment, we wish to have control over the electrode potential but, in practice, the voltage we apply between the electrodes is partly consumed in the ohmic loss and diffusion potential. In the light of Eq. (3.7) and (3.9) it is obvious that increasing the solution conductivity κ, we can reduce these losses. These leads us to the concept of a **supporting electrolyte** and a **trace-ion** to which we return later on.

The analysis of a binary system is useful in revealing some important aspects of ionic transport. Let's consider again an electrolyte $A_{\upsilon_1}B_{\upsilon_2}$ dissociating completely to ions A^{z_1} and B^{z_2}. Hence, $c_1 = \upsilon_1 c_{12}$ and $c_2 = \upsilon_2 c_{12}$ where c_{12} is the electrolyte concentration. Electroneutrality reads $\upsilon_1 z_1 + \upsilon_2 z_2 = 0$. Let's write the Nernst-Planck equations for the both species:

$$\begin{cases} \vec{j}_1 = -D_1 \nabla c_1 - z_1 f c_1 D_1 \nabla \phi + \vec{v} c_1 \\ \vec{j}_2 = -D_2 \nabla c_2 - z_2 f c_2 D_2 \nabla \phi + \vec{v} c_2 \end{cases} \Rightarrow \begin{cases} \dfrac{\vec{j}_1}{D_1} = -\upsilon_1 \nabla c_{12} - \upsilon_1 z_1 c_{12} f \nabla \phi + \vec{v} \dfrac{\upsilon_1 c_{12}}{D_1} \\ \dfrac{\vec{j}_2}{D_2} = -\upsilon_2 \nabla c_{12} - \upsilon_2 z_2 c_{12} f \nabla \phi + \vec{v} \dfrac{\upsilon_2 c_{12}}{D_2} \end{cases} \tag{3.10}$$

Summing above equations gives

$$\frac{\vec{j}_1}{D_1} + \frac{\vec{j}_2}{D_2} = -(\upsilon_1 + \upsilon_2) \nabla c_{12} + \vec{v} c_{12} \left(\frac{\upsilon_1}{D_1} + \frac{\upsilon_2}{D_2} \right) \tag{3.11}$$

Realizing that $\vec{j}_2 = \left(\vec{I}/F - z_1 \vec{j}_1 \right) / z_2$ it is obtained after some algebra that

$$\vec{j}_1 = -\upsilon_1 \frac{(\upsilon_1 + \upsilon_2) D_1 D_2}{\upsilon_1 D_2 + \upsilon_2 D_1} \nabla c_{12} + \frac{\upsilon_2 D_1}{\upsilon_1 D_2 + \upsilon_2 D_1} \frac{\vec{I}}{z_1 F} + \upsilon_1 \nabla c_{12} \vec{v} \tag{3.12}$$

Identifying the following groups of variables,

$$D_{12} = \frac{\upsilon_{12} D_1 D_2}{\upsilon_2 D_1 + \upsilon_1 D_2} \quad \Leftrightarrow \quad \frac{\upsilon_{12}}{D_{12}} = \frac{\upsilon_1}{D_1} + \frac{\upsilon_2}{D_2} \quad ; \quad \upsilon_{12} = \upsilon_1 + \upsilon_2 \tag{3.13}$$

$$t_1 = \frac{\upsilon_2 D_1}{\upsilon_1 D_2 + \upsilon_2 D_1} \quad ; \quad t_2 = 1 - t_1 \tag{3.14}$$

we can write the transport equation as earlier presented in the Fickian approach:

$$\vec{j}_i = -\upsilon_i D_{12} \nabla c_{12} + \frac{t_i \vec{I}}{z_i F} + \upsilon_i \vec{v}\, c_{12} \quad ; \quad i = 1,2 \tag{3.15}$$

Eq. (3.13) is known as the **Nernst-Hartley** equation, and D_{12} is the diffusion coefficient of the electrolyte. It shows that an ion cannot diffuse by itself, but it is coupled to a counter-ion. This is true also in a multicomponent system although the equations become very complicated. That is also the reason why single ionic mobilities cannot be measured from the conductance data of electrolytes (home exercise). Instead, looking at D_{12} and the transport number t_1 that are both measurable quantities,

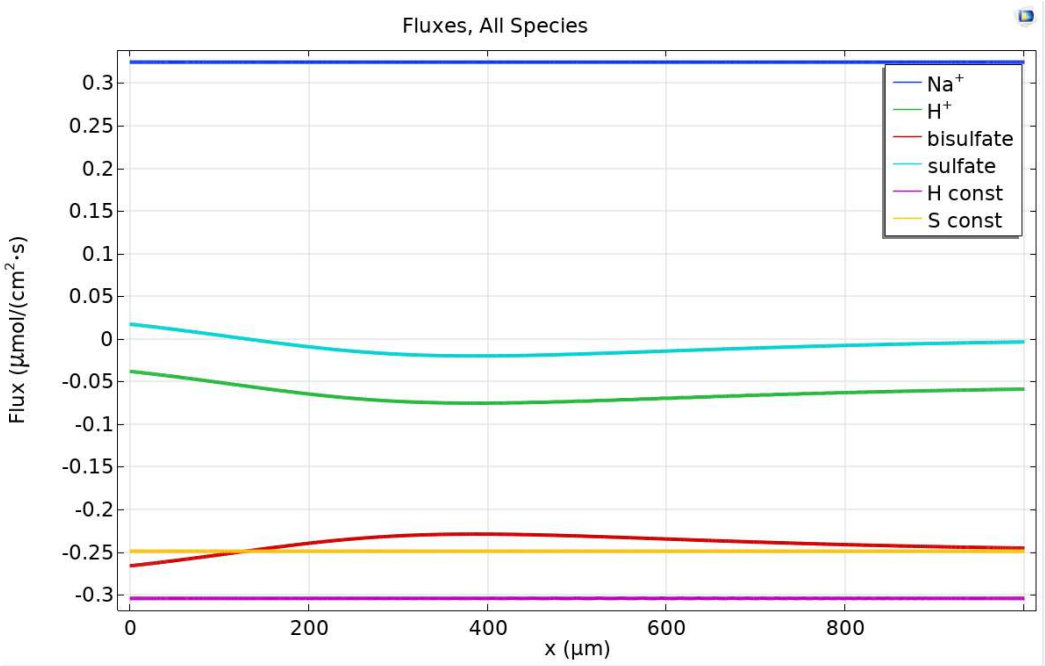
$$\frac{D_{12}}{t_1} = \left(1 + \frac{\upsilon_1}{\upsilon_2}\right) D_2 \tag{3.16}$$

Example: The diffusion coefficient of H^+ is $9.31 \cdot 10^{-5}$ cm^2/s, that of Cl^- $2.03 \cdot 10^{-5}$ cm^2/s and that of SO_4^{2-} $1.06 \cdot 10^{-5}$ cm^2/s. From the Nernst-Hartley equation, the diffusion coefficient of HCl is $3.33 \cdot 10^{-5}$ cm^2/s and that of H_2SO_4 $2.59 \cdot 10^{-5}$ cm^2/s. This shows that these anions slow down the transfer of H^+, while H^+ is accelerating the transfer of the slower anions. This is exactly the effect of diffusion potential, reflected in the values of the electrolyte diffusion coefficients.

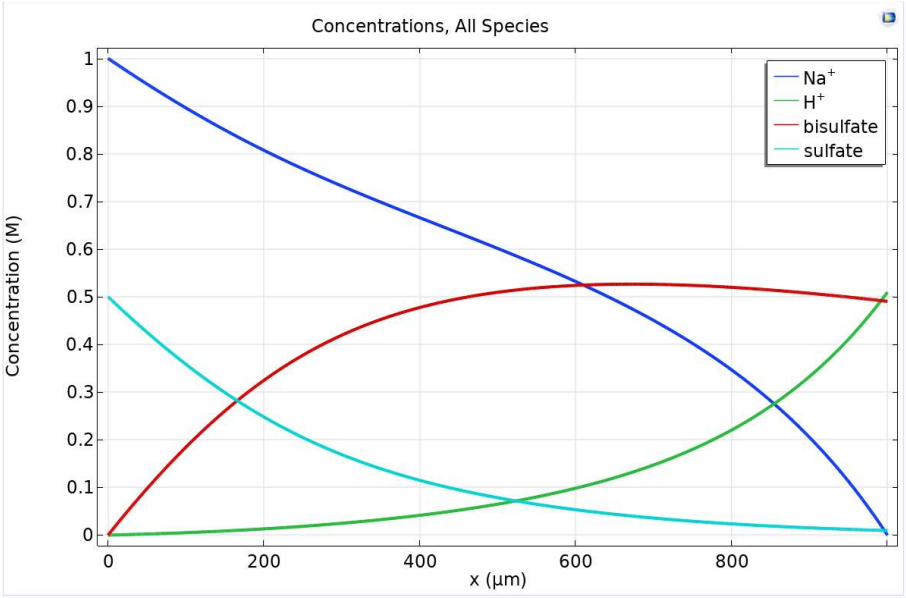
Due to inherent coupling of ionic fluxes via long-range electrostatic interactions the Nernst-Planck equation works very nicely, except in very concentrated solutions. In very concentrated solutions ion-ion interactions become more important, which requires another approach.

Weak electrolytes

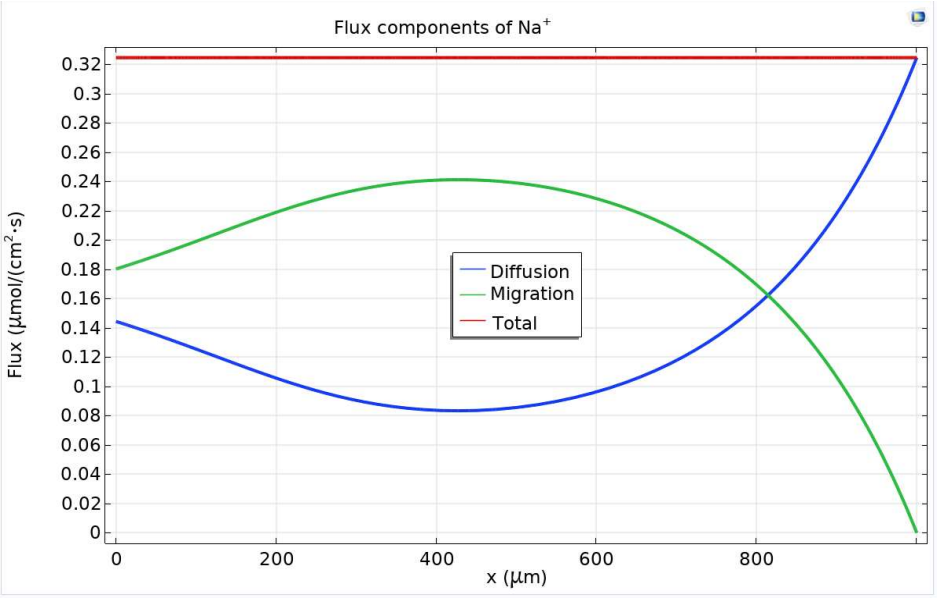
Transport of weak electrolytes has an extra issue to take into account. Consider H_2SO_4: the first proton dissociates completely, making a bisulfate anion. Since pK_a of bisulfate is ca. 2, at pH < 2 it remains as bisulfate and at pH > 2 it dissociates to sulfate and another proton. Instead of calculating (if even possible!) the fluxes of bisulfate and sulfate separately, the only meaningful quantity is their sum, the flux of **sulfate constituent**. Protons are transferring as free protons and as bisulfate and, analogously, the only meaningful quantity is the sum of their fluxes, the flux of **proton constituent**.



At steady-state, the flux of a species $\iint_S \vec{j}_i^{\,m} \cdot dS$ across a surface *S* is constant (in 1D calculations also the flux density $\vec{j}_i^{\,m}$ is constant). That does not apply to ions of weak electrolytes, because their degree of dissociation varies along the concentration profile; only the fluxes of ion constituents are constant. A Comsol model of this situation is presented aside. On the left, 0.5 M Na_2SO_4, on the right, 0.5 M H_2SO_4. Current density 50 mA/cm² (from left to right). Positive flux means flow from left to right (negative naturally vice verse).



Concentration profiles of all the ions in the previously mentioned system.



The total sodium flux is constant, as it should, but the individual flux components in the Nernst-Planck equation vary as a function of position.

Although the ionic fluxes are not constant, the definition of the electric current density (eq. (2.24) or (3.6)) still applies. As the constituent fluxes are constant, it is possible to express the current density in their terms:

$$\vec{I} = F\left(\vec{j}_{Na^+} + \vec{j}_{H^+} - \vec{j}_{HSO_4^-} - 2\vec{j}_{SO_4^{2-}}\right) = F\left(\vec{j}_{Na^+} + \vec{J}_H - 2\vec{J}_S\right)$$

$$\vec{J}_H = \vec{j}_{H^+} + \vec{j}_{HSO_4^-} \quad ; \quad \vec{J}_S = \vec{j}_{HSO_4^-} + \vec{j}_{SO_4^{2-}} \qquad (3.17)$$

Stefan-Maxwell (friction coefficient) approach

In concentrated solutions the most natural approach is to consider the interactions between all species in the solution. When a solute is transferring through a solution it collides with solvent molecules and other solutes, causing friction to its transfer. The frictional force depends on the strength of the interaction, characterized with a friction coefficient K'_{ij}, the number of collisions, *viz* the number of particles (like in the kinetic gas theory), expressed in mole fractions, and the **relative speed** of the colliding particles. At steady-state, the driving force of transfer is equal but opposite to the friction forces:

driving force + frictional force = 0

If we consider diffusion, the driving force could be the concentration gradient, leading to

$$\nabla c_i = \sum_j K'_{ij}\, x_j (\vec{v}_j - \vec{v}_i) \tag{3.18}$$

We can develop further the left hand side:

$$\nabla c_i = c_i \nabla \ln c_i = \frac{c_i}{RT} \nabla \mu_i = \sum_j K'_{ij}\, x_j (\vec{v}_j - \vec{v}_i) \quad \Leftrightarrow \quad c_i \nabla \mu_i = RT \sum_j K'_{ij}\, x_j (\vec{v}_j - \vec{v}_i) \tag{3.19}$$

In order to proceed, let's consider first the simplest case, a binary solution. From eq. (3.19),

$$c_1 \nabla \mu_1 = K_{10} (\vec{v}_0 - \vec{v}_1) \tag{3.20}$$

where the solvent mole fraction x_0 and RT are included in K_{10}.

In the Hittorf reference frame the solute flux is expressed as

$$\vec{j}_1^{\mathrm{H}} = c_1(\vec{v}_1 - \vec{v}_0) = -\frac{c_1^2}{K_{10}}\nabla\mu_1 = -\frac{\overline{D}_{10}c_1}{RTx_0}\nabla\mu_1 \qquad (3.21)$$

The above equation introduces the Stefan-Maxwell diffusion coefficient

$$\overline{D}_{10} = RT\frac{c_1 x_0}{K_{10}} = \frac{c_1}{K'_{10}} \qquad (3.22)$$

At moderately dilute solutions $x_0 \approx 1$ and $\nabla\mu_1 \approx \mathrm{RT}\nabla\ln c_1 = \mathrm{RT}(\nabla c_1/c_1)$. Hence,

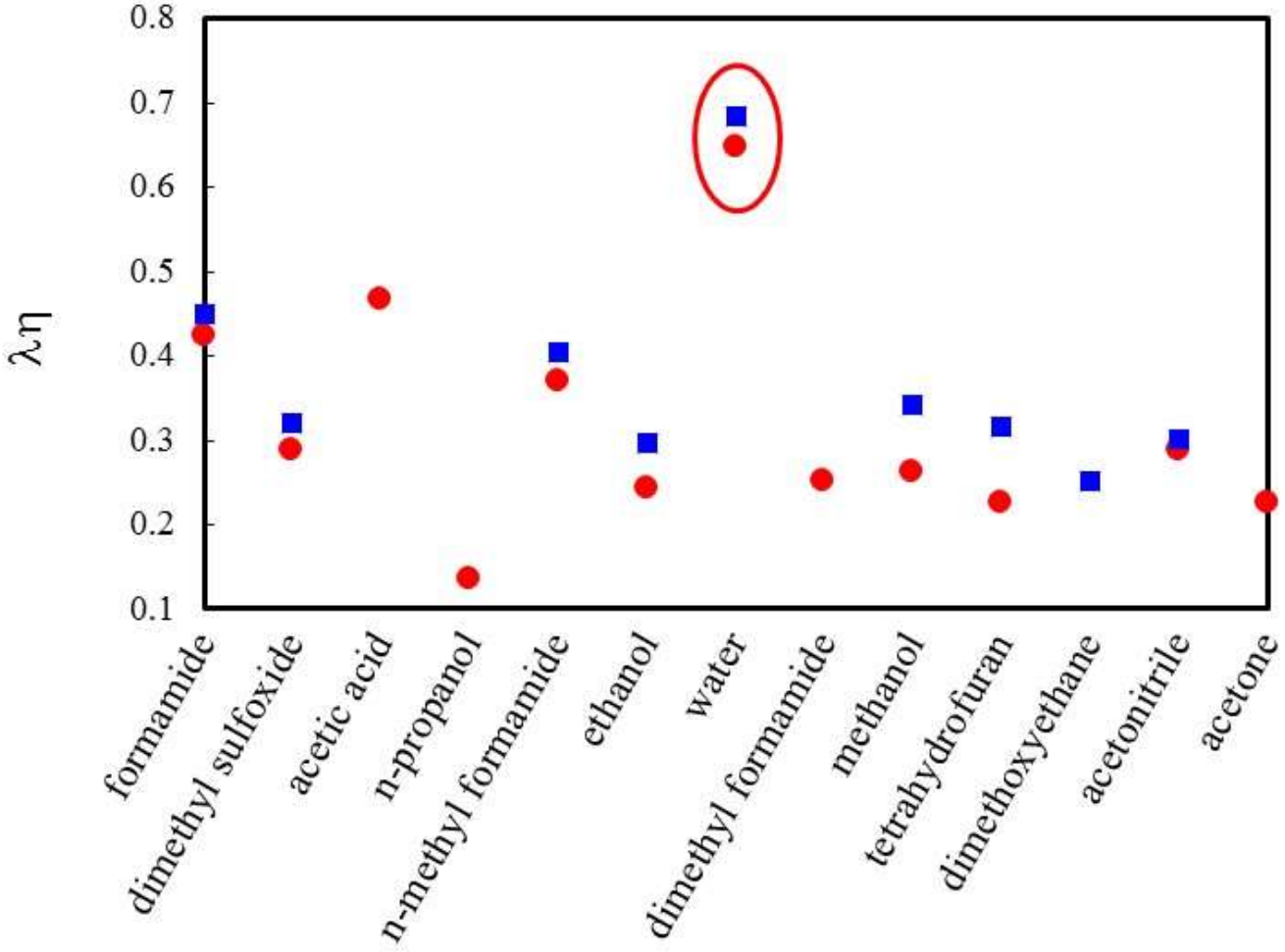
$$\vec{j}_1^{\mathrm{H}} = -\overline{D}_{10}\nabla c_1 \qquad (3.23)$$

At moderately dilute solutions the Fickian (D_1) and Stefan-Maxwell diffusion coefficients thus are equal but differ at high concentrations significantly. For a spherical particle the Stokes' law gives the friction coefficient as $K_{10} \approx 6\pi R_1 \eta N_{\mathrm{A}} c_1$, leading to

$$D_1 \approx \frac{RT}{6\pi R_1 \eta N_{\mathrm{A}}} = \frac{k_{\mathrm{B}}T}{6\pi R_1 \eta} \qquad (3.24)$$

where R_1 is the particle radius and N_{A} the Avogadro's number. Although Stokes' law was derived for macroscopic particles it works surprisingly well also to molecules and ions (but not for ions in water, see next page).

Validity of Stokes' law for K^+ (●) and Cs^+ (■) in various solvents.



$$\lambda_k = \frac{F^2 z_k^2 D_k}{RT}$$

Considering a binary electrolyte solution where a salt dissociates into υ_1 cations with the charge number z_1 and υ_2 anions with the charge number z_2 ($\upsilon_1 z_1 + \upsilon_2 z_2 = 0$), the transport equations become

$$\begin{aligned} c_1 \nabla \tilde{\mu}_1 &= K_{10}(\vec{v}_0 - \vec{v}_1) + K_{12}(\vec{v}_2 - \vec{v}_1) \\ c_2 \nabla \tilde{\mu}_2 &= K_{20}(\vec{v}_0 - \vec{v}_2) + K_{21}(\vec{v}_1 - \vec{v}_2) \end{aligned} \tag{3.25}$$

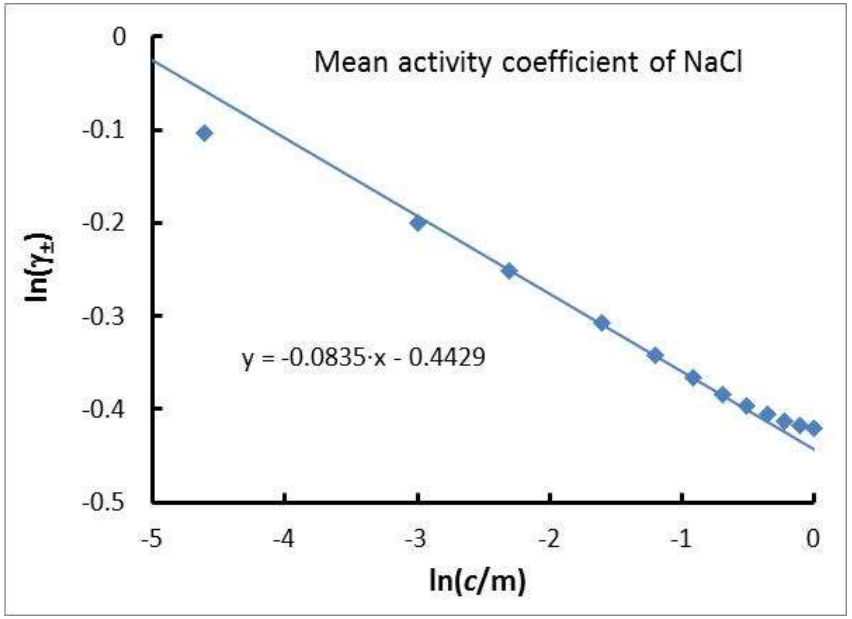
Also here Onsager's reciprocal theorem applies, $K_{ij} = K_{ji}$. Electric current density (in Hittorf reference) is

$$\vec{I} = F\left(z_1 \vec{j}_1^{\,\mathrm{H}} + z_2 \vec{j}_2^{\,\mathrm{H}}\right) = F\left[c_1 z_1 (\vec{v}_1 - \vec{v}_0) + c_2 z_2 (\vec{v}_2 - \vec{v}_0)\right] = F c_1 z_1 \left[(\vec{v}_1 - \vec{v}_0) - (\vec{v}_2 - \vec{v}_0)\right] = F c_1 z_1 (\vec{v}_1 - \vec{v}_2) \tag{3.26}$$

Eq. (3.26) once again shows that electric current is independent of the reference velocity (here $\vec{v}_0$). In the absence of current $\vec{v}_1 = \vec{v}_2$. In that case the flux becomes straight from eq. (3.20), replacing μ with $\tilde{\mu}$:

$$\vec{j}_i^{\,\mathrm{H}} = -\frac{\overline{D}_{i0} c_i}{RT x_0}\left(\nabla \mu_i + z_i F \nabla \phi\right) = -\frac{\overline{D}_{i0} c_i}{x_0}\left[\nabla \ln(\gamma_i c_i) + z_i f \nabla \phi\right] = -\frac{\overline{D}_{i0}}{x_0}\left[\nabla c_i \left(1 + \frac{\nabla \ln(\gamma_i)}{\nabla \ln(c_i)}\right) + z_i c_i f \nabla \phi\right] \tag{3.27}$$

The above equation resembles the Nernst-Planck equation with the exception of the activity coefficient correction $\partial \ln(\gamma_i)/\partial \ln(c_i)$. As the plot in the following page shows, this correction term can reach up to ca. 10% significance in the case of NaCl in water. In principle, this correction could be imposed also in the Nernst-Planck equation.



In the case of pure conduction, in the absence of concentration gradients, the equations are

$$z_1 c_1 F\nabla\phi = K_{10}(\vec{v}_0 - \vec{v}_1) + K_{12}(\vec{v}_2 - \vec{v}_1)$$
$$z_2 c_2 F\nabla\phi = K_{20}(\vec{v}_0 - \vec{v}_2) + K_{21}(\vec{v}_1 - \vec{v}_2) \qquad (3.28)$$

This pair of equations can be treated as follows:

$$\frac{z_1 c_1 F\nabla\phi}{K_{10}} = \vec{v}_0 - \vec{v}_1 + \frac{K_{12}}{K_{10}}(\vec{v}_2 - \vec{v}_1)$$
$$-\frac{z_1 c_1 F\nabla\phi}{K_{20}} = \vec{v}_0 - \vec{v}_2 + \frac{K_{21}}{K_{20}}(\vec{v}_1 - \vec{v}_2) \qquad (3.29)$$

Subtracting eqs. (3.29) from each other gives (note Onsager's theorem)

$$z_1 c_1 F\nabla\phi\left(\frac{1}{K_{10}} + \frac{1}{K_{20}}\right) = (\vec{v}_2 - \vec{v}_1)\left(1 + \frac{K_{12}}{K_{10}} + \frac{K_{12}}{K_{20}}\right) = -\frac{\vec{I}}{z_1 c_1 F}\left[1 + K_{12}\left(\frac{1}{K_{10}} + \frac{1}{K_{20}}\right)\right] \qquad (3.30)$$

Solving $\vec{I}$ in the form of Ohm's law, $\vec{I} = -\kappa\nabla\phi$, the conductivity κ is reached as (textbook eq. (2.147))

$$\kappa = \frac{z_1^2 F^2 c_1^2}{K_{12} + (1/K_{20} + 1/K_{10})^{-1}} = \frac{z_1^2 F^2 c_1^2 (K_{10} + K_{20})}{K_{10}K_{20} + K_{12}(K_{10} + K_{20})} \qquad (3.31)$$

In the presence of both concentration gradients and electric current the textbook presents the appropriate equations, (2.150) – (2.158), pp. 68-69.

An interesting example is ionic liquids, i.e. solvents that are formed from cations and anions. In that case the solvent is also a charge carrier and dissolving any electrolyte in an ionic liquid makes the system at least ternary, more often quaternary. The transport of an electrolyte in an ionic liquid is hardly described with the Nernst-Planck equation or Fick's laws. Only when the concentration of an electrolyte is very low compared with the ionic liquid these approaches can be applied (with care).

In the case of an ionic liquid alone, no concentration gradients can exist, and the only possible transport process is electric conduction:

$$z_1 c_1 F \nabla\phi = K_{12}(\vec{v}_2 - \vec{v}_1)$$
$$z_2 c_2 F \nabla\phi = K_{21}(\vec{v}_1 - \vec{v}_2) \qquad (3.32)$$

Note that these equations are actually identical because $z_2 c_2 = -z_1 c_1$ and $K_{12} = K_{21}$. From either of these equations it is obtained:

$$z_1 c_1 F \nabla\phi = -K_{12} \frac{\vec{I}}{z_1 c_1 F} \qquad (3.33)$$

$$\vec{I} = -\frac{z_1^2 c_1^2 F^2}{K_{12}} \nabla\phi = -\frac{F^2}{RT} \overline{D}_{12} z_1^2 c_1 \nabla\phi \qquad (3.34)$$

Hence, the only difference to the Nernst-Planck equation is the Stefan-Maxwell diffusion coefficient. Measuring the conductivity of an ionic liquid the friction coefficient K_{12} and $\overline{D}_{12}$ can be determined.

If we have an ionic liquid A^+B^- (c_{12}) and an electrolyte A^+Cl^-(c_{13}), the following expression can be derived after lengthy algebra*

$$\kappa = F^2 \frac{K_{23}c_1^2 + K_{13}c_2^2 + K_{12}c_3^2}{K_{12}K_{13} + K_{12}K_{23} + K_{13}K_{23}} \qquad t_3 = \frac{K_{12}c_3^2}{K_{23}c_1^2 + K_{13}c_2^2 + K_{12}c_3^2} \qquad D_3 = \frac{M_{12}c_1}{M_{12}c_2 + M_{13}c_3} \frac{t_3 c_2^2}{K_{12}} \left[\frac{v_{13}}{v_{23}} \left(\frac{\partial \mu_2}{\partial c_2} \right) + \left(\frac{\partial \mu_3}{\partial c_3} \right) \right]$$

where M_{ij} and v_{ij} are the molar mass and molar volume of the electrolyte, respectively. Only at the limit $c_3 \ll c_2$ the transport equation of Cl^-reduce to the form of Fick's law (or Nernst-Planck with electric current), and D_3 takes the form

$$D_3 \approx \frac{RTc_{13}}{K_{13} + K_{23}}$$

The problem of the Stefan-Maxwell formalism is obvious: the values of the friction coefficients are merely unknown. Yet, it is the most appropriate approach as it considers all the interactions in the solution. It is clear that the treatment of multi-ionic systems becomes extremely difficult. Therefore, the Nernst-Planck equation has received the major role in the study of ionic transport. Stefan-Maxwell approach is used in modelling the transport of, e.g. mixtures of hydrocarbons in petrochemical industry.

* T. Vainikka et al. Electrochimica Acta 87 (2013) 739-748.