Poisson-Plank-Nerst Equation

1 potential and concentration: Poisson equation

The Gauss law gives the following relation

$$\begin{aligned}
\mathbf{D} &= \epsilon_0\epsilon\mathbf{E} && (1)\\
\mathbf{E} &= -\nabla\phi && (2)\\
\mathrm{div}\mathbf{D} &= \rho && (3)\\
\nabla(\epsilon_0\epsilon\mathbf{E}) &= -\epsilon_0\nabla(\epsilon(\mathbf{r})\nabla\phi(\mathbf{r})) = \rho(\mathbf{r}) && (4)\\
\int \mathbf{D}\cdot\mathbf{n}dS &= \int \rho dV && (5)\\
\rho &= F\sum_i z_i c_i && (6)
\end{aligned}$$

Faraday constant F / C mol^{-1}, valnce z_i (no dimension), concentration c_i / mol m^{-3}, charge density, ρ / C m^{-3}. Later we will reformulate 1-D case.

2 Diffusion and Migration

The electrochemical potential $\tilde{\mu}_i$ is given by $\tilde{\mu}_i = \mu_i^{\ominus} + RT\ln a_i + z_iF\phi$. The force on i-species is given by

$$\begin{aligned}
\vec{f_i} &= -\nabla\tilde{\mu}_i && (7)\\
&= -RT\nabla\ln a_i - z_iF\nabla\phi && (8)\\
&= -\frac{RT}{a_i}\nabla a_i - z_iF\nabla\phi && (9)\\
&= -\frac{RT}{\gamma_i c_i}(\gamma_i\nabla c_i + c_i\nabla\gamma_i) - z_iF\nabla\phi && (10)\\
&= -RT\left(\frac{1}{c_i} + \frac{1}{\gamma_i}\frac{d\gamma_i}{dc_i}\right)\nabla c_i - z_iF\nabla\phi && (11)
\end{aligned}$$

In the last equation we used

$$c_i\nabla\gamma_i = c_i\frac{d\gamma_i}{dc_i}\nabla c_i \qquad (12)$$

If we assume that the activity coefficietn γ_i is constant

$$\vec{f_i} = -\frac{RT}{c_i}\nabla c_i - z_iF\nabla\phi \qquad (13)$$

In general the velocity is proportional to the force in the viscous fluid,

$$\vec{v}_i = B_i \vec{f}_i \tag{14}$$

The flux J_i (mol m^{-2} s^{-1}) of the i-species is also generally given by

$$\vec{J}_i = \vec{v}_i c_i = B_i c_i \vec{f}_i \tag{15}$$

2.1 diffusion

When there is no potential, the force by diffusion is given by

$$\vec{f}_i^{\text{diff}} = -RT\left(\frac{1}{c_i} + \frac{1}{\gamma_i}\frac{d\gamma_i}{dc_i}\right)\nabla c_i \tag{16}$$

$$\vec{J}_i^{\text{diff}} = -B_i c_i RT\left(\frac{1}{c_i} + \frac{1}{\gamma_i}\frac{d\gamma_i}{dc_i}\right)\nabla c_i \tag{17}$$

The Fick's first law gives the flux J_i^{diff} (mol m^{-2} s^{-1}) by diffusion

$$\vec{J}_i^{\text{diff}} = -D_i \nabla c_i \tag{18}$$

Then for diffusion coefficient we have

$$D_i = B_i RT\left(1 + \frac{c_i}{\gamma_i}\frac{d\gamma_i}{dc_i}\right) = D_i^0\left(1 + \frac{c_i}{\gamma_i}\frac{d\gamma_i}{dc_i}\right) \tag{19}$$

The relationship between the force and the flux by diffusion is given by

$$\vec{J}_i^{\text{diff}} = B_i c_i \vec{f}_i^{\text{diff}} = \frac{D_i}{RT(1 + \frac{c_i}{\gamma_i}\frac{d\gamma_i}{dc_i})} c_i \vec{f}_i^{\text{diff}} = \frac{D_i^0}{RT} c_i \vec{f}_i^{\text{diff}} \tag{20}$$

2.2 migration

For the migration, the force by migration is given by

$$\vec{f}_i^{\text{mig}} = -z_i F \nabla\phi \tag{21}$$

The flux J_i (mol m^{-2} s^{-1}) is generally given by

$$\vec{J}_i = \vec{v}_i c_i \tag{22}$$

and the mobility u_i is given by the electric field E

$$u_i \equiv \frac{\vec{v}_i^{\text{mig}}}{E} \tag{23}$$

$$\vec{J}_i^{\text{mig}} = \vec{v}_i^{\text{mig}} c_i = c_i u_i \vec{E} = -c_i u_i \nabla\phi \tag{24}$$

$$= \frac{c_i u_i}{z_i F} \vec{f}_i^{\text{mig}} \tag{25}$$

2.3 Nernst-Einstein equation

If the force is balanced and the total flux becomes zero

$$\vec{f}_i^{\rm diff} = -\vec{f}_i^{\rm mig} \quad (26)$$

$$\vec{J}_i = \vec{J}_i^{\rm diff} + \vec{J}_i^{\rm mig} = 0 \quad (27)$$

$$= \frac{D_i}{RT(1+\frac{c_i}{\gamma_i}\frac{d\gamma_i}{dc_i})} c_i \vec{f}_i^{\rm diff} + \frac{c_i u_i}{z_i F}\vec{f}_i^{\rm mig} = \left(\frac{D_i c_i}{RT(1+\frac{c_i}{\gamma_i}\frac{d\gamma_i}{dc_i})} - \frac{c_i u_i}{z_i F}\right)\vec{f}_i^{\rm diff} \quad (28)$$

$$\frac{c_i u_i}{z_i F} = \frac{D_i c_i}{RT(1+\frac{c_i}{\gamma_i}\frac{d\gamma_i}{dc_i})} = \frac{D_i^0 c_i}{RT} \quad (29)$$

$$u_i = \frac{z_i F D_i^0}{RT} \quad (30)$$

We call the last equation is new Nernst-Einstein equation. Then we can write the flux

$$\vec{J}_i = -D_i \nabla c_i - \frac{z_i F D_i^0}{RT} c_i \nabla \phi \quad (31)$$

This is the new Nernst-Plank equation. The equation of continuity is given by

$$0 = \frac{\partial c_i}{\partial t} + {\rm div}\vec{J}_i \quad (32)$$

Finally we can get

$$\frac{\partial c_i}{\partial t} = \nabla(D_i \nabla c_i + \frac{z_i F D_i^0}{RT} c_i \nabla \phi) \quad (33)$$

$$= \nabla D_i \nabla c_i + D_i \nabla^2 c_i + \frac{z_i F D_i^0}{RT}(\nabla c_i \nabla \phi + c_i \nabla^2 \phi) \quad (34)$$

$$c_i = c_i(\mathbf{r}, t), \quad \gamma_i = \gamma_i(c_i), \quad \frac{d\gamma_i}{dc_i} \equiv \gamma_i' = \gamma_i'(c_i), \quad \frac{d^2\gamma_i}{dc_i^2} \equiv \gamma_i'' = \gamma_i''(c_i), \quad (35)$$

$$\nabla \gamma_i^{-1} = \frac{\partial \gamma_i^{-1}}{\partial c_i}\nabla c_i = \frac{\partial \gamma_i^{-1}}{\partial \gamma_i}\frac{\partial \gamma_i}{\partial c_i}\nabla c_i = -\gamma_i^{-2}\gamma_i' \nabla c_i \quad (36)$$

$$\nabla \gamma_i' = \frac{d\gamma_i'}{dc_i}\nabla c_i = \gamma_i'' \nabla c_i \quad (37)$$

$$\nabla D_i = \nabla(D_i^0 c_i \gamma_i^{-1}\gamma_i') \quad (38)$$

$$= D_i^0(\gamma_i^{-1}\gamma_i' \nabla c_i + c_i \gamma_i' \nabla \gamma_i^{-1} + c_i \gamma_i^{-1}\nabla \gamma_i') \quad (39)$$

$$= D_i^0[\gamma_i^{-1}\gamma_i' - \gamma_i^{-2} c_i (\gamma_i')^2 + c_i \gamma_i^{-1}\gamma_i''] \nabla c_i \quad (40)$$

$$\nabla D_i \nabla c_i = D_i^0[\gamma_i^{-1}\gamma_i' - \gamma_i^{-2} c_i (\gamma_i')^2 + c_i \gamma_i^{-1}\gamma_i''](\nabla c_i)^2 \quad (41)$$

3 1D case

When the diffusion and the potential is planar and the force is only in x direction, and the dielectric constant is uniform except the boundary. First we set

$$c_i = c_i(x, t), \quad \gamma_i = \gamma_i(c_i), \quad \frac{d\gamma_i}{dc_i} \equiv \gamma_i' = \gamma_i'(c_i), \quad \frac{d^2\gamma_i}{dc_i^2} \equiv \gamma_i'' = \gamma_i''(c_i), \quad (42)$$

$$\text{for both sides of the phase} \tag{43}$$

$$-\epsilon_0\epsilon\frac{\partial^2\phi(x,t)}{\partial x^2} = F\sum_i z_i c_i(x,t) \tag{44}$$

$$\text{at interface} \tag{45}$$

$$\epsilon_0\epsilon_- \left.\frac{\mathrm{d}\phi}{\mathrm{d}z}\right|_- - \epsilon_0\epsilon_+ \left.\frac{\mathrm{d}\phi}{\mathrm{d}z}\right|_+ = \sigma \tag{46}$$

$$\text{if there is no specificadsorption at the interface}, \sigma = 0, \text{ then} \tag{47}$$

$$\epsilon_- \left.\frac{\mathrm{d}\phi}{\mathrm{d}z}\right|_- = \epsilon_+ \left.\frac{\mathrm{d}\phi}{\mathrm{d}z}\right|_+ \tag{48}$$

$$\frac{\partial c_i}{\partial t} = D_i^0(1+\frac{c_i}{\gamma_i}\gamma_i')\frac{\partial^2 c_i(x,t)}{\partial x^2} + D_i^0[\gamma_i^{-1}\gamma_i' - \gamma_i^{-2}c_i(\gamma_i')^2 + c_i\gamma_i^{-1}\gamma_i'']\left(\frac{\partial c_i}{\partial x}\right)^2 \tag{49}$$

$$+\frac{z_iFD_i^0}{RT}\left(\frac{\partial c_i(x,t)}{\partial x}\frac{\partial\phi(x,t)}{\partial x} + c_i(x,t)\frac{\partial^2\phi(x,t)}{\partial x^2}\right) \tag{50}$$

$$\text{if } \gamma_i' = 0, \text{ then} \tag{51}$$

$$\frac{\partial c_i}{\partial t} = D_i^0\frac{\partial^2 c_i(x,t)}{\partial x^2} \tag{52}$$

$$+\frac{z_iFD_i^0}{RT}\left(\frac{\partial c_i(x,t)}{\partial x}\frac{\partial\phi(x,t)}{\partial x} + c_i(x,t)\frac{\partial^2\phi(x,t)}{\partial x^2}\right) \tag{53}$$