BE.430 Recitation:
Summary of the Electrochemical Subsystem

Adapted from A. Grodzinsky
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Equations governing the electrochemical system (and mechanical subsystem):

(1) $\underline{N}_i = -D_i \nabla c_i + \frac{z_i}{|z_i|} u_i c_i \underline{E} + c_i \underline{v}_{fl}$ (Molar flux constitutive Equation)

(2) $\frac{\partial c_i}{\partial t} = -\nabla \cdot \underline{N}_i + R_i$ (Species Conservation)

(3) $\nabla \cdot \varepsilon \underline{E} = \rho_e = \overline{\rho}_m + \sum_i z_i F c_i$ (Gauss' Law)

(4) $\underline{E} = -\nabla \Phi$ (Faraday's Law)

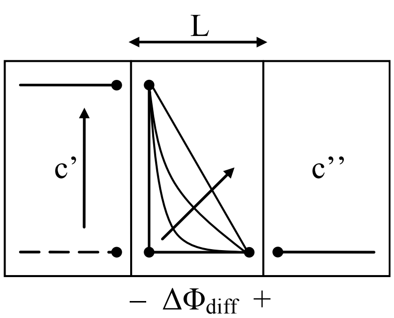
(5) $\nabla \cdot \underline{J} = -\frac{\partial \rho_e}{\partial t}$ (Conservation of Charge)

(6) $\underline{J} = \sigma \underline{E} + (\quad) \nabla c_i + (\quad) \underline{v}_{fl}$ (Current Density flux constitutive equation)

(7) $\rho \frac{D\underline{v}_{fl}}{Dt} = -\nabla p + \mu \nabla^2 \underline{v}_{fl} + \rho_e \underline{E} + \ldots$ (Conservation of Momentum)

(8) $\nabla \cdot \underline{v}_{fl} = 0$ (Conservation of Mass)

[I.] *Non-equilibrium/Non-steady* transport across *neutral* membrane/tissue (§1.6 – 2.3)



- $K_{\text{part}} = 1$ (neglect sterics)

Keywords:

- **Coupled Diffusion**
  Due to unequal diffusivities of electrolyte species $D_+ \neq D_-$
  Leads to self-induced electric field "E_{self}"
- **Charge Relaxation**
  Electroneutrality for length scales of $L >> 1/\kappa$

$$(3) \Rightarrow \overline{\rho}_m + z(\overline{c}_+ - \overline{c}_-) \simeq 0$$
$$\Rightarrow \overline{c}_{Na} \simeq \overline{c}_{Na} \equiv \overline{c}$$

Combine (1) + (2) + (3) for $\overline{c}_+, \overline{c}_-$ (coupled diffusion)

$$\frac{\partial \overline{c}}{\partial t} = \left(\frac{2D_+D_-}{D_+ + D_-}\right) \nabla^2 \overline{c} - \left(\frac{D_+D_-}{D_+ + D_-}\right) \nabla \cdot (\overline{c}_+ - \overline{c}_-) \frac{\underline{E}}{RT/F}$$ where the last term is negligible.

$$(5) \rightarrow \frac{\partial \rho_e}{\partial t} = -\nabla \cdot F\left(u_+ + u_-\right)\bar{c}\,\underline{E} - \nabla \cdot F\left(D_+ + D_-\right)\nabla \bar{c}$$

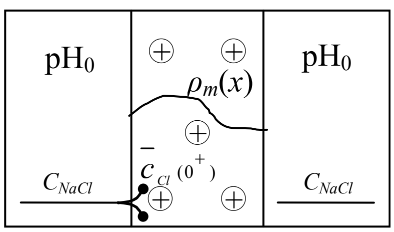
$$= -\nabla \cdot \underline{J}_{mig} \qquad\qquad -\nabla \cdot \underline{J}_{diff}$$

Steady-state "Diffusion Potential" (not Nernst potential)

$$\Delta\Phi_{diff} = -\frac{RT}{|z|F}\left(\frac{D_+ - D_-}{D_+ + D_-}\right)\ln\left(\frac{c''}{c'}\right)$$

which leads to "E_{self}" due to difference in diffusivities

[II.] Donnan *Equilibrium* for *Charged Membrane*



$$\boxed{\begin{array}{c}\dfrac{\partial}{\partial t} = 0 \\ N_i \equiv 0\end{array}}$$

(**Boltzmann distribution** of ionic species)

$$\Rightarrow \bar{c}_i\left(x\right) = c_i^{bath} e^{-z_i F \phi(x)/RT}$$

$$\Rightarrow \left(\frac{\bar{c}_i\left(x\right)}{\bar{c}_i}\right)^{\frac{1}{z_i}} = const$$

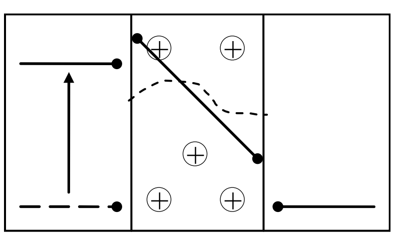
and electroneutrality:

$$\left(\bar{\rho}_m\left(x\right) + \sum \bar{c}_i\left(x\right) F z_i\right) \simeq 0$$

Donnan potential:

$$\Phi\left(x\right) - \Phi_{ref}^{bath} = -\frac{RT}{|z|F}\ln\left(\frac{\bar{c}_i\left(x\right)}{c_i^{bath}}\right)$$ ("Nernst-like" expression)

[III.] *Non-Equilibrium* transport across *charged* tissue



Types of problems:

Steady or non-steady

To find $\bar{c}\left(x,t\right)$

- use (1), (2), (3), (4)
- use Donnan equilibrium only at boundaries

  Use of Donnan equilibrium at boundaries are valid since formation charge equilibrium occurs much quicker than the electrodiffusion process.

Please, look at problem 2.7.1 for a thorough understanding of electrodiffusion and non-equilibrium transport across a charged tissue.