

Reaction Diffusion system with ^{ext} electric field.

We are considering a system of electrolytes coming from a symmetric salt.

To analyse the system, we first consider the continuity equation,

$$\frac{\partial C_s}{\partial t} + \nabla \cdot \vec{N}_s = r$$

where C_s is the concentration, \vec{N}_s the flux of particles and r the reaction rate.

a typical model for the flux in such context is

$$\vec{N}_s = D \left(\nabla \cdot C_s + \frac{s z F}{RT} C_s \nabla \phi \right)$$

where

D : Diffusion coef.

s : sign of the charged the electrolyte

z : valence of the electrolyte

$F := e N_A$: Faraday's constant

$R := k_B N_A$: Gases constant.

T : temperature

ϕ : Potential

is considered as a border condition such that

$$\left[\frac{\partial G_s}{\partial t} + \nabla \cdot \vec{N}_s \right] \Big|_{x=\delta} = \begin{cases} \tau, & s > 0 \\ 0, & s < 0. \end{cases}$$

Steady State solution:

we first consider

$$\frac{\partial G_s}{\partial t} = 0$$

which yields

$$\nabla \cdot \vec{N}_s = 0$$

$$N_s = \text{constant.}$$

we get the following two equations:

$$\begin{aligned} \frac{\partial G_+(x)}{\partial x} + \frac{z_+ F}{RT} C_+(x) \nabla \phi &= \tau \\ \frac{\partial C_-(x)}{\partial x} - \frac{z_- F}{RT} C_-(x) \nabla \phi &= 0 \end{aligned}$$

and

$$\nabla^2 \phi = -\frac{1}{\epsilon} z_+ F (C_+(x) - C_-(x))$$

as,

~~$\phi(x) =$~~

$$\phi''(x) = -\frac{zF}{RT} C_b \left(e^{-\frac{zF}{RT} \phi(x)} - e^{\frac{zF}{RT} \phi(x)} \right)$$

we define,

$$\frac{zF}{RT} \phi(x) = \psi$$

as the dimensionless potential

$$\psi''(x) = -\frac{z^2 F^2}{R^2 T^2} C_b \left(e^{-\psi(x)} - e^{+\psi(x)} \right)$$

let

$$K^2 = 2 \frac{z^2 F^2}{R^2 T^2} C_b$$

$$\psi''(x) = -\frac{K^2}{2} \left(e^{-\psi(x)} - e^{+\psi(x)} \right)$$

$$\psi''(x) = -K^2 \sinh(\psi(x))$$

Define the Dimensionless potential as

$$\psi = \frac{zF}{RT} \phi$$

~~Also, we must take into account~~

From the Poisson's equation:

$$\phi''(x) = -\frac{zF}{RT} (C_+(x) - C_-(x))$$

⊗ No reaction case,

$$\frac{\partial C_s(x)}{\partial x} = -\frac{szF}{RT} C_s(x) \nabla \phi$$

$$\frac{dC_s(x)}{C_s(x)} = -\frac{szF}{RT} \phi'(x) dx$$

$$\Rightarrow \ln\left(\frac{C_s(x)}{C_s(0)}\right) = -\frac{szF}{RT} \int_0^x \phi'(x) dx$$
$$= -\frac{szF}{RT} (\phi(x) - \phi(0))$$

$$\Rightarrow C_s(x) = C_s(0) e$$

Defining $\phi(0) = 0$, we get

$$C_s(x) = C_{s(0)} e^{-\frac{szF}{RT} \phi(x)}$$

redefine the system in terms of these variables,

$$\begin{aligned}\frac{\partial C_+(x)}{\partial x} + C_+(x) \nabla \psi(x) &= r \\ \frac{\partial C_-(x)}{\partial x} - C_-(x) \nabla \psi(x) &= 0 \\ \psi'' &= -K^2 \sinh(K\psi(x))\end{aligned}$$

we want to get the additional lengthscale

$$z = Kx \rightarrow x = z/K$$

$$\Rightarrow \frac{\partial C_s(x)}{\partial z} = \frac{\partial C_s}{\partial x} \frac{\partial x}{\partial z} = C_s'(x) \cdot \frac{1}{K}$$

$$\frac{\partial \psi}{\partial z} = \frac{\partial \psi}{\partial x} \cdot \frac{\partial x}{\partial z} = \psi'(x) \frac{1}{K}$$

Thus,

$$C_s'(x) = K C_s'(z)$$

$$\psi'(x) = K \psi'(z)$$

Also

$$\frac{\partial^2 \psi}{\partial z^2} = \frac{\partial}{\partial z} \left(\psi'(x) \frac{1}{K} \right) = \frac{1}{K} \frac{\partial \psi'}{\partial x} \cdot \frac{\partial x}{\partial z} = \frac{1}{K^2} \psi''(x)$$

$$\psi''(x) = K^2 \psi''(z)$$

here,

$$C'_s(x) = K C'_s(z)$$

$$\psi'(x) = K \psi'(z)$$

$$\psi''(x) = K^2 \psi''(z)$$

Now the range of integration is:

$$x = (0, \delta) \rightarrow z = (0, K\delta)$$

where $K\delta \sim 1$.

thus, we rewrite the equations in terms of these variables.

$$K C'_+(z) + K C_+(z) \psi'(z) = r$$

$$K C'_-(z) - K C_-(z) \psi'(z) = 0$$

$$K^2 \psi''(z) = -K^2 \sinh(\psi(z))$$

$$\Rightarrow \begin{cases} C'_+(z) + C_+(z) \psi'(z) = r \\ C'_-(z) - C_-(z) \psi'(z) = 0 \\ \psi''(z) = -\sinh(\psi(z)) \end{cases}$$

$$r^2 = \frac{r}{K}$$

$$\frac{d}{dz} (e^{\psi(z)} \psi(z)) = \tilde{r} e^{\psi(z)}$$

$$\int_0^z dz' (e^{\psi(z')} \psi(z'))' = \int_0^z dz' \tilde{r} e^{\psi(z')}$$

$$e^{\psi(z)} \psi(z) - e^{\psi(0)} \psi(0) = \tilde{r} \int_0^z dz' e^{\psi(z')}$$

$$\psi(z) = e^{-\psi(z)} \left(c_b + \tilde{r} \int_0^z dz' e^{\psi(z')} \right)$$

thus we get :

$$\psi_-(z) = c_b e^{\psi(z)}$$

$$\psi_+(z) = c_b e^{-\psi(z)} \left(1 + \frac{\tilde{r}}{c_b} \int_0^z dz' e^{\psi(z')} \right)$$

$$K^2 \psi''(z) = -\frac{(2\tilde{r})^2}{\epsilon AT} (\psi_+(z) - \psi_-(z))$$

That is

$$\begin{aligned} \psi_-(z) &= c_b e^{\psi(z)} \\ \psi_+(z) &= c_b e^{-\psi(z)} \left(1 + \frac{\tilde{r}}{c_b} \int_0^z dz' e^{\psi(z')} \right) \\ \psi''(z) &= -(\psi_+(z) - \psi_-(z)) \end{aligned}$$