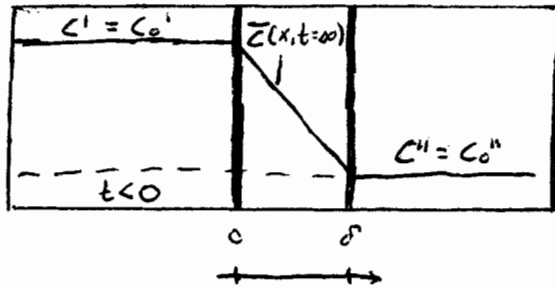


Problem 2.2.1 - Coupled Diffusion Step Response:
Characteristic Diffusion Time



$$\bar{D}^* = \frac{2\bar{D}_+\bar{D}_-}{\bar{D}_+ + \bar{D}_-}$$

from example 2.2.2.

a) (1.6.3.) $\bar{\Gamma}_+ = +\bar{u}_+\bar{c}_+\underline{E} - \bar{D}_+\nabla\bar{c}_+$

(1.6.4.) $\bar{\Gamma}_- = -\bar{u}_-\bar{c}_-\underline{E} - \bar{D}_-\nabla\bar{c}_-$

valid in absence of
bulk convection.

($\bar{c}_+ = \bar{c}_+(x)$, $\bar{c}_- = \bar{c}_-(x)$)

We found in 2.2.3 that

$$\frac{d\Phi(x)}{dx} = -\frac{zF(\bar{D}_+ - \bar{D}_-)\frac{d\bar{c}_0(x)}{dx}}{zF(\bar{u}_+ + \bar{u}_-)\bar{c}_0(x)}$$

where $\underline{E} = -\frac{d\Phi(x)}{dx}\underline{e}_x$

Substituting these equations into 1.6.3 and 1.6.4, we obtain

$$\bar{\Gamma}_+ = \frac{\bar{u}_+ zF(\bar{D}_+ - \bar{D}_-)\bar{c}_+ \frac{d\bar{c}_0(x)}{dx}}{zF(\bar{u}_+ + \bar{u}_-)\bar{c}_0(x)} - \bar{D}_+ \frac{d\bar{c}_+}{dx}$$

$$\bar{\Gamma}_- = \frac{\bar{u}_- zF(\bar{D}_+ - \bar{D}_-)\bar{c}_- \frac{d\bar{c}_0(x)}{dx}}{zF(\bar{u}_+ + \bar{u}_-)\bar{c}_0(x)} - \bar{D}_- \frac{d\bar{c}_-}{dx}$$

We assume electroneutrality during diffusion of a binary electrolyte,
s.t. $\bar{c}_+ = \bar{c}_- \approx \bar{c}_0(x) = \bar{c}(x)$

$$\Rightarrow \bar{\Gamma}_+ = \bar{u}_+ \left(\frac{\bar{D}_+ - \bar{D}_-}{\bar{u}_+ + \bar{u}_-} \right) \frac{d\bar{c}(x)}{dx} - \bar{D}_+ \frac{d\bar{c}(x)}{dx}$$

$$\bar{\Gamma}_- = -\bar{u}_- \left(\frac{\bar{D}_+ - \bar{D}_-}{\bar{u}_+ + \bar{u}_-} \right) \frac{d\bar{c}(x)}{dx} - \bar{D}_- \frac{d\bar{c}(x)}{dx}$$

Using the Einstein relation

$$u_i = \frac{D_i z_i F}{RT} \quad (1.2.2.)$$

$$\begin{aligned} \Rightarrow \bar{\Gamma}_+ &= \left[\bar{D}_+ \left(\frac{\bar{D}_+ - \bar{D}_-}{\bar{D}_+ + \bar{D}_-} \right) - \bar{D}_+ \right] \frac{d\bar{c}}{dx} \\ &= \left[\frac{\bar{D}_+ (\bar{D}_+ - \bar{D}_-) - \bar{D}_+ (\bar{D}_+ + \bar{D}_-)}{\bar{D}_+ + \bar{D}_-} \right] \frac{d\bar{c}}{dx} \\ &= - \left(\frac{2\bar{D}_+ \bar{D}_-}{\bar{D}_+ + \bar{D}_-} \right) \frac{d\bar{c}}{dx} = -\bar{D}^* \frac{d\bar{c}}{dx} \quad \text{qed.} \end{aligned}$$

Similarly,

$$\begin{aligned} \bar{\Gamma}_- &= \left[\bar{D}_- \left(\frac{\bar{D}_+ - \bar{D}_-}{\bar{D}_+ + \bar{D}_-} \right) - \bar{D}_- \right] \frac{d\bar{c}}{dx} \\ &= \left[\frac{\bar{D}_- (\bar{D}_+ - \bar{D}_-) - \bar{D}_- (\bar{D}_+ + \bar{D}_-)}{\bar{D}_+ + \bar{D}_-} \right] \frac{d\bar{c}}{dx} \\ &= - \left(\frac{2\bar{D}_+ \bar{D}_-}{\bar{D}_+ + \bar{D}_-} \right) \frac{d\bar{c}}{dx} = -\bar{D}^* \frac{d\bar{c}}{dx} \end{aligned}$$

Transient diffusion problem

$$\begin{aligned} c_+^I = c_-^I &= (c_0^I - c_0^{II}) u_{-1}(t) + c_0^I \\ c_+^{II} = c_-^{II} &= c_0^{II} \end{aligned} \quad u_{-1}(t) \begin{cases} 0 & t < 0 \\ 1 & t \geq 0 \end{cases}$$

b) Derive the diff eq. for 1-D transient diffusion of a binary electrolyte

$$\frac{\partial \bar{c}(x,t)}{\partial t} = \bar{D}^* \frac{\partial^2 \bar{c}(x,t)}{\partial x^2}$$

Assume quasi-neutrality and neglect convection.

We start with the continuity equations for both positive and negative species given by 1.6.1 and 1.6.2

$$\begin{aligned} \frac{\partial \bar{c}_+}{\partial t} + \underline{v} \cdot \frac{\partial \bar{c}_+}{\partial \underline{x}} &= -\frac{\partial \bar{\Gamma}_+}{\partial \underline{x}} \Rightarrow \frac{\partial \bar{c}_+}{\partial t} = -\frac{\partial \bar{\Gamma}_+}{\partial \underline{x}} \\ \frac{\partial \bar{c}_-}{\partial t} + \underline{v} \cdot \frac{\partial \bar{c}_-}{\partial \underline{x}} &= -\frac{\partial \bar{\Gamma}_-}{\partial \underline{x}} \Rightarrow \frac{\partial \bar{c}_-}{\partial t} = -\frac{\partial \bar{\Gamma}_-}{\partial \underline{x}} \end{aligned}$$

neglecting
convection

Recalling 1.6.3 and 1.6.4

$$\begin{aligned} \bar{\Gamma}_+ &= +\bar{u}_+ \bar{c}_+ \underline{E} - \bar{D}_+ \frac{\partial \bar{c}_+}{\partial \underline{x}} \\ \bar{\Gamma}_- &= -\bar{u}_- \bar{c}_- \underline{E} - \bar{D}_- \frac{\partial \bar{c}_-}{\partial \underline{x}} \end{aligned}$$

Substituting 1.6.3 and 1.6.4 into 1.6.1 and 1.6.2, respectively,

$$\frac{\partial \bar{c}_+}{\partial t} = \frac{\partial}{\partial \underline{x}} (\bar{D}_+ \frac{\partial \bar{c}_+}{\partial \underline{x}}) - \frac{\partial}{\partial \underline{x}} (\bar{u}_+ \bar{c}_+ \underline{E}_x) \quad (a)$$

$$\frac{\partial \bar{c}_-}{\partial t} = \frac{\partial}{\partial \underline{x}} (\bar{D}_- \frac{\partial \bar{c}_-}{\partial \underline{x}}) + \frac{\partial}{\partial \underline{x}} (\bar{u}_- \bar{c}_- \underline{E}_x) \quad (b)$$

Multiply (a) by \bar{D}_- and (b) by \bar{D}_+ and add them:

$$\frac{\partial}{\partial t} (\bar{D}_- \bar{c}_+ + \bar{D}_+ \bar{c}_-) = \frac{\partial}{\partial \underline{x}} (\bar{D}_- \bar{D}_+ [\frac{\partial \bar{c}_+}{\partial \underline{x}} + \frac{\partial \bar{c}_-}{\partial \underline{x}}]) - \frac{\partial}{\partial \underline{x}} [\frac{E}{RT} \bar{D}_- \bar{D}_+ (\bar{c}_+ - \bar{c}_-) \underline{E}]$$

where we made the use of the Einstein relation

$$\frac{D_i}{u_i} = \frac{RT}{|z_i| F}$$

We assume quasi-neutrality such that 1.6.20, 1.6.23 is valid.

\Rightarrow the last term is negligible and with

$$\bar{c}_+ \approx \bar{c}_- \equiv \bar{c}$$

$$\frac{\partial}{\partial t} ((\bar{D}_+ + \bar{D}_-) \bar{c}) = \frac{\partial}{\partial x} (2\bar{D}_- \bar{D}_+ \frac{\partial \bar{c}}{\partial x})$$

$$\Rightarrow \frac{\partial \bar{c}}{\partial t} = \underbrace{\frac{2\bar{D}_- \bar{D}_+}{\bar{D}_+ + \bar{D}_-}}_{D^*} \cdot \frac{\partial^2 \bar{c}}{\partial x^2} \quad \text{qed.}$$

c) Boundary conditions

1. $\bar{c}(x=0, t) = c'_0$
2. $\bar{c}(x=\delta, t) = c''_0$

Initial condition:

$$\bar{c}(x, t=0^+) = 0$$

d) Let $\bar{c}(x, t) = \hat{c}(x, t) + \bar{c}_0(x)$

The steady-state solution:

$$\frac{\partial \bar{c}_0(x)}{\partial t} = 0 = \frac{\partial^2 \bar{c}_0(x)}{\partial x^2}$$

$$\Rightarrow \bar{c}_0(x) = Ax + B$$

With B.C.s

$$1. \bar{c}_0(x=0) = c_0' = A \cdot 0 + B \Rightarrow B = c_0'$$

$$2. \bar{c}_0(x=\delta) = c_0'' = A \cdot \delta + c_0' \Rightarrow A = \frac{c_0'' - c_0'}{\delta}$$

$$\Rightarrow \bar{c}_0(x) = (c_0'' - c_0') \frac{x}{\delta} + c_0'$$

The transient solution:

$$\frac{\partial \hat{c}(x,t)}{\partial t} = \frac{\partial^2 \hat{c}(x,t)}{\partial x^2}$$

w/ B.C.s

$$1. \hat{c}(x=0,t) = \bar{c}(x=0,t) - \bar{c}_0(0) = c_0' - c_0' = 0$$

$$2. \hat{c}(x=\delta,t) = \bar{c}(x=\delta,t) - \bar{c}_0(\delta) = c_0'' - c_0'' = 0$$

and I.C.

$$\hat{c}(x,t=0^+) = \bar{c}(x,t=0^+) - \bar{c}_0(x) = (c_0' - c_0'') \frac{x}{\delta} - c_0'$$

We found in Homework #2 that the complete solution gives

$$c(x,t) = c_0' + (c_0'' - c_0') \frac{x}{\delta} + \sum_{n=1}^{\infty} \frac{2}{n\pi} [c_0'' \cos(n\pi) - c_0'] \sin \frac{n\pi x}{\delta} e^{-t/\tau_n}$$

$$\text{where } \tau_n = \frac{\delta^2}{D^* n^2 \pi^2}$$

$$e) \tau_{n=1} = \frac{\delta^2}{D^* \pi^2}$$

Compute \bar{D}^* from Table 1.2.1 (diffusivities in infinite dilution)

$$D_{Na^+} = 1.33 \cdot 10^{-5} \frac{\text{cm}^2}{\text{s}}$$

$$D_{Cl^-} = 2.03 \cdot 10^{-5} \frac{\text{cm}^2}{\text{s}}$$

$$\bar{D}^* = \frac{2\bar{D}_{Na^+}\bar{D}_{Cl^-}}{\bar{D}_{Na^+} + \bar{D}_{Cl^-}} = \frac{2 \cdot 1.33 \cdot 10^{-5} \frac{\text{cm}^2}{\text{s}} \cdot 2.03 \cdot 10^{-5} \frac{\text{cm}^2}{\text{s}}}{1.33 \cdot 10^{-5} \frac{\text{cm}^2}{\text{s}} + 2.03 \cdot 10^{-5} \frac{\text{cm}^2}{\text{s}}}$$

$$= 1.61 \cdot 10^{-5} \frac{\text{cm}^2}{\text{s}}$$

For $\delta = 10 \text{ nm}$,

$$\tau_{n=1} = \frac{(10 \cdot 10^{-6} \text{ cm})^2}{1.61 \cdot 10^{-5} \frac{\text{cm}^2}{\text{s}} \cdot \pi^2}$$

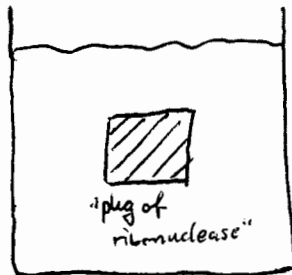
$$= \underline{\underline{6.3 \cdot 10^{-7} \text{ s}}}$$

For $\delta = 0.5 \text{ mm}$

$$\tau_{n=1} = \frac{(0.05 \text{ cm})^2}{1.61 \cdot 10^{-5} \frac{\text{cm}^2}{\text{s}} \cdot \pi^2}$$

$$= \underline{\underline{15.7 \text{ s}}}$$

Problem 2.4.3 - Electrical conductivity as a measure of charge density $\bar{\rho}_m$ and of the isoelectric point (pI) of the material



(b) and (c)
adapted from
A. Grodzinsky

a) Find $\bar{\Phi}$ in terms of $\bar{\rho}_m$, \bar{u}_{Na} , \bar{u}_{Cl} , C_0 and other constants

One of the many statements Donnan Equilibrium makes is

$$2.4.17 \quad \Delta\Phi_D = -\frac{1}{z_i} \cdot \frac{RT}{F} \ln \frac{\bar{c}_i}{c_i}$$

At equilibrium, the Donnan potential determines the inside and outside concentrations of species i . For the case of NaCl solution, each ion species in equilibrium across the phase boundary satisfies the relation

$$\left(\frac{\bar{c}_{Na^+}}{c_{Na^+}} \right) = \left(\frac{\bar{c}_{Na^+}}{c_0} \right) = \left(\frac{c_0}{\bar{c}_{Cl^-}} \right) = \text{const.} = e^{-F\Delta\Phi_D/RT}$$

$$\longrightarrow \bar{c}_{Na^+} \bar{c}_{Cl^-} = c_0^2 \quad (1)$$

Electroneutrality inside the bulk RNase exists:

$$\bar{\rho}_m + F\bar{c}_{Na^+} - F\bar{c}_{Cl^-} = 0 \quad (\text{neglecting } C_{H^+}, C_{OH^-})$$

$$\Rightarrow \bar{c}_{Cl^-} = \left(\frac{\bar{\rho}_m}{F} \right) + \bar{c}_{Na^+} \quad (2)$$

(2) and (1) give

$$\bar{c}_{Na^+} \left(\frac{\bar{p}_m}{F} + \bar{c}_{Na^+} \right) = c_0^2$$

$$\Rightarrow \bar{c}_{Na^+}^2 + \frac{\bar{p}_m}{F} \bar{c}_{Na^+} - c_0^2 = 0$$

$$\Rightarrow \bar{c}_{Na^+} = -\frac{\bar{p}_m}{2F} + \sqrt{\frac{\bar{p}_m^2}{4F^2} + c_0^2} \quad (3)$$

Similarly, $\bar{c}_{Cl^-} = +\frac{\bar{p}_m}{2F} + \sqrt{\frac{\bar{p}_m^2}{4F^2} + c_0^2}$

From 1.2.9.

$$\bar{G} = \sum_i |z_i| F \bar{u}_i \bar{c}_i$$

$$= F \bar{u}_{Na^+} \bar{c}_{Na^+} + F \bar{u}_{Cl^-} \bar{c}_{Cl^-}$$

$$= F \left[\left(-\frac{\bar{p}_m}{2F} + \frac{\sqrt{\bar{p}_m^2 + 4F^2 c_0^2}}{2F} \right) \bar{u}_{Na^+} + \left(\frac{\bar{p}_m}{2F} + \frac{\sqrt{\bar{p}_m^2 + 4F^2 c_0^2}}{2F} \right) \bar{u}_{Cl^-} \right]$$

$$\Rightarrow \boxed{2\bar{G} = \bar{p}_m (\bar{u}_+ + \bar{u}_-) + \sqrt{\bar{p}_m^2 + 4F^2 c_0^2} (\bar{u}_+ + \bar{u}_-)}$$

$$\begin{aligned} \bar{u}_+ &= \bar{u}_{Na^+} \\ \bar{u}_- &= \bar{u}_{Cl^-} \end{aligned}$$

b) Find \bar{p}_m as a function of $\bar{G}, c_0, \bar{u}_+, \bar{u}_-$

$$\text{Let } \alpha = \bar{u}_+ - \bar{u}_- \quad \beta = (\bar{u}_+ + \bar{u}_-)$$

$$\Rightarrow 2\bar{G} = -\bar{p}_m \alpha + \beta \sqrt{\bar{p}_m^2 + 4F^2 c_0^2}$$

$$\left(\frac{2\bar{G}}{\beta} + \bar{p}_m \frac{\alpha}{\beta} \right)^2 = \bar{p}_m^2 + 4F^2 c_0^2$$

$$\frac{4\bar{G}^2}{\beta^2} + 4\frac{\alpha}{\beta^2} \bar{p}_m \bar{G} + \left(\frac{\alpha}{\beta} \right)^2 \bar{p}_m^2 = \bar{p}_m^2 + 4F^2 c_0^2$$

$$\Rightarrow \bar{\rho}_m^2 \left(1 - \left(\frac{\alpha}{\beta}\right)^2\right) - 4 \frac{\alpha}{\beta^2} \bar{z} \bar{\rho}_m + (4F^2 c_0^2 - \frac{4\bar{z}^2}{\beta^2}) = 0$$

$$\bar{\rho}_m = \frac{\left(\frac{2\bar{z}\alpha}{\beta^2}\right) \pm \sqrt{\left(\frac{2\bar{z}\alpha}{\beta^2}\right)^2 - \left(1 - \left(\frac{\alpha}{\beta}\right)^2\right)\left(4F^2 c_0^2 - \frac{4\bar{z}^2}{\beta^2}\right)}}{\left[1 - \left(\frac{\alpha}{\beta}\right)^2\right]}$$

$$\bar{\rho}_m = \frac{2\alpha\bar{z} \pm \sqrt{\alpha^2\beta^2 F^2 c_0^2 - \beta^4 F^2 c_0^2 + \beta^2 \bar{z}^2}}{\beta^2 - \alpha^2}$$

$$\text{where } \alpha = \bar{u}_+ - \bar{u}_- \quad (\beta^2 - \alpha^2 = 4\bar{u}_+ \bar{u}_-)$$

$$\beta = \bar{u}_+ + \bar{u}_-$$

Note: For $\alpha = 0$ (as in case of KCl or KNO_3)
such that $\bar{u}_+ \approx \bar{u}_- \equiv \bar{u}$

$$\Rightarrow \bar{\rho}_m = \sqrt{\frac{4\bar{z}^2}{\beta^2} - 4F^2 c_0^2}$$

$$\bar{\rho}_m = \sqrt{\left(\frac{2\bar{z}}{\bar{u}_+ + \bar{u}_-}\right)^2 - 4F^2 c_0^2}$$

$$\bar{\rho}_m^2 = F^2 (\bar{c}_+ + \bar{c}_-)^2 - 4F^2 c_0^2$$

$$\Rightarrow (\bar{c}_+ + \bar{c}_-)^2 \approx \frac{\bar{\rho}_m^2}{F^2} + 4c_0^2$$

Minimum in conductivity \bar{z} will occur when $\bar{\rho}_m$ is a small negative number (for $\alpha \neq 0$) or when $\bar{\rho}_m = 0$ ($\alpha = 0$) (see appendix)

Therefore, the choice of sign in front of $\sqrt{\quad}$ depends on the sign of α . Since $\bar{z}(\alpha) = \mp \sqrt{\quad}$ when $\bar{\rho}_m = 0$.

$\Rightarrow \alpha > 0$, then we use + sign & vice versa. For NaCl, $\alpha < 0 \Rightarrow$ we use \ominus .

c) The isoelectric point for RNase can be inferred to be 9.5 from the titration figure. The I.E.P is the pH at which the net charge in the RNase is zero, i.e. $\bar{P}_m \sim 0$.

If c_0 is small enough, then $\bar{C}_{\text{counterion}} \approx \bar{P}_m(\text{pH})$ for enough away from the I.E.P., and $\bar{\zeta} \approx F(\bar{u}\bar{C})_{\text{counterion}}$. Therefore, $\bar{\zeta}$ will look like the absolute magnitude of the titration curve for $\text{pH} \gtrsim \text{I.E.P.}$ by just enough pH units such that $|\frac{\bar{P}_m}{F}| \gg c_0$.



(Compare to titration curve)

Appendix: Minimum $\bar{\mathcal{E}}$

From part (a)

$$2\bar{\mathcal{E}} = \alpha\bar{\rho}_m + \beta(\bar{\rho}_m^2 + 4F^2c_0^2)^{1/2}$$

$$\Rightarrow 2\frac{\partial\bar{\mathcal{E}}}{\partial\bar{\rho}_m} = \alpha + \frac{\beta}{2} \cdot \frac{2\bar{\rho}_m}{(\bar{\rho}_m^2 + 4F^2c_0^2)^{1/2}} = 0 \quad \text{for minimum}$$

$$\Rightarrow \bar{\rho}_m = -\frac{\alpha}{\beta} [\bar{\rho}_m^2 + 4F^2c_0^2]^{1/2}$$

$$\bar{\rho}_m^2 (1 - (\frac{\alpha}{\beta})^2) = (\frac{\alpha}{\beta})^2 4F^2c_0^2$$

$$\Rightarrow \bar{\rho}_m = \pm \frac{2(\frac{\alpha}{\beta})Fc_0}{[1 - (\frac{\alpha}{\beta})^2]^{1/2}}$$

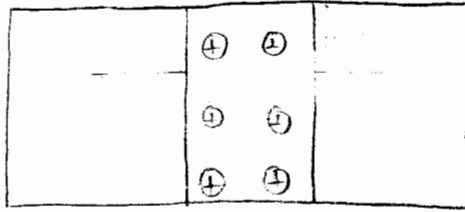
$$= -\frac{2(\frac{\alpha}{\beta})Fc_0}{[1 - (\frac{\alpha}{\beta})^2]^{1/2}}$$

These equations should show the same sign. So $\bar{\rho}_m < 0$ for both equality to hold.

For KCl, $\bar{u}_+ \approx \bar{u}_- \Rightarrow \alpha = 0 \Rightarrow$ minimum at $\bar{\rho}_m = 0$

For $\alpha \neq 0$, minimum occurs for small negative value of $\bar{\rho}_m$

a)



$$\text{Given: } \frac{P_{mo}}{F} = -[COO^-]_0 + [NH_3^+]_0$$

pH < 6 where $[NH_3^+]_0 \approx \text{constant}$

$$[COO^-](x,t) \propto [H^+]$$

Parameter Definitions:

$[H^+]$ = concentration of unbound (free) H^+ ions

$[COO^-]$ = concentration of free carboxyl groups

$[COOH]$ = concentration of neutralized carboxyl groups

$H_B = [COOH] =$ concentration of bound H^+

$G_T = [COO^-] + [COOH] =$ concentration of binding sites.

Initially: Baths $\rightarrow [Na^+] = [Cl^-] = C_0$

Membrane $\rightarrow [H^+] \ll [Cl^-]$

Continuity Equations Inside the Membrane:

$$\frac{\partial [Na^+]}{\partial t} = D_{Na^+} \frac{\partial^2 [Na^+]}{\partial x^2} - \bar{u}_{Na^+} [Na^+] \frac{\partial E_x}{\partial x} - \bar{u}_{Na^+} \frac{\partial [Na^+]}{\partial x} E_x$$

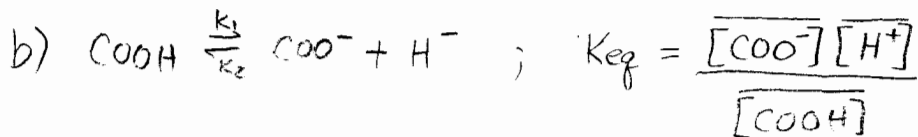
$$\frac{\partial [Cl^-]}{\partial t} = D_{Cl^-} \frac{\partial^2 [Cl^-]}{\partial x^2} + \bar{u}_{Cl^-} [Cl^-] \frac{\partial E_x}{\partial x} + \bar{u}_{Cl^-} \frac{\partial [Cl^-]}{\partial x} E_x$$

$$\frac{\partial [H^+]}{\partial t} + \frac{\partial H_B}{\partial t} = D_{H^+} \frac{\partial^2 [H^+]}{\partial x^2} - \bar{u}_{H^+} [H^+] \frac{\partial E_x}{\partial x} - \bar{u}_{H^+} \frac{\partial [H^+]}{\partial x} E_x$$

\uparrow Free \uparrow Binding Term
 Total H^+

Gauss's Law $\Rightarrow \nabla \cdot \Sigma E = \rho_m$

$$ID: \frac{\partial}{\partial x} (\Sigma E) = \bar{\rho}_m + F ([Na^+] - [Cl^-] + [H^+]) \\ = F ([NH_3^+] + [Na^+] + [H^+] - [Cl^-] - [COO^-])$$



$$H_B = [COOH] = \frac{[COO^-][H^+]}{K_{eq}}$$

$$H_B = \frac{\{C_T - [COOH]\} [H^+]}{K_{eq}}$$

$$H_B = \frac{(C_T - H_B) [H^+]}{K_{eq}}$$

$$H_B = \frac{C_T [H^+]}{K_{eq} + [H^+]} \Rightarrow \frac{\partial H_B}{\partial t} = \frac{\partial}{\partial t} \left\{ \frac{C_T [H^+]}{K_{eq} + [H^+]} \right\}$$

c) $\bar{\rho}_m \gg F [H^+]_{bath} \Rightarrow$ membrane has high net positive charge which will favor the negative counter-ions more than the positive co-ions.

$\therefore \overline{[H^+]}$ & $\overline{[Na^+]}$ will be low, while $\overline{[Cl^-]}$ will be high.

$$\frac{\partial \overline{[H^+]}}{\partial t} + \frac{\partial H_B}{\partial t} = D_{H^+} \frac{\partial^2 \overline{[H^+]}}{\partial x^2} - \bar{u}_{H^+} \frac{\partial}{\partial x} (\overline{[H^+] E}) \rightarrow \approx 0.$$

Because $\overline{[H^+]}$ is a minority carrier, it will see the membrane as neutral where the negative counter-ions have shielded positive fixed charges. Therefore, the H^+ ions will simply diffuse across. & $\bar{u}_{H^+} \frac{\partial}{\partial x} (\overline{[H^+] E})$ becomes negligible.

$$\frac{\partial [\overline{H^+}]}{\partial t} + \frac{\partial}{\partial t} \left(\frac{C_T [\overline{H^+}]}{K_{eq} + [\overline{H^+}]} \right) = D_{H^+} \frac{\partial^2 [\overline{H^+}]}{\partial x^2}$$

$$\frac{\partial [\overline{H^+}]}{\partial t} + \frac{C_T \frac{\partial [\overline{H^+}]}{\partial t} (K_{eq} + [\overline{H^+}]) - \frac{\partial [\overline{H^+}]}{\partial t} C_T [\overline{H^+}]}{(K_{eq} + [\overline{H^+}])^2} = D_{H^+} \frac{\partial^2 [\overline{H^+}]}{\partial x^2}$$

$$\frac{\partial [\overline{H^+}]}{\partial t} \left\{ 1 + \frac{C_T (K_{eq} + [\overline{H^+}]) - C_T [\overline{H^+}]}{(K_{eq} + [\overline{H^+}])^2} \right\} = D_{H^+} \frac{\partial^2 [\overline{H^+}]}{\partial x^2}$$

$$\frac{\partial [\overline{H^+}]}{\partial t} \left\{ 1 + \frac{C_T K_{eq}}{(K_{eq} + [\overline{H^+}])^2} \right\} = D_{H^+} \frac{\partial^2 [\overline{H^+}]}{\partial x^2}$$

$$\frac{\partial [\overline{H^+}]}{\partial t} = \underbrace{\frac{D_{H^+}}{\left\{ 1 + \frac{C_T K_{eq}}{(K_{eq} + [\overline{H^+}])^2} \right\}}}_{D_{eff}} \frac{\partial^2 [\overline{H^+}]}{\partial x^2}$$

D_{eff}

d) $D_{eff} = \frac{D_{H^+}}{\left\{ 1 + \frac{C_T K_{eq}}{(K_{eq} + [\overline{H^+}])^2} \right\}}$; if $[\overline{H^+}]_0 \ll K_{eq}$, $D_{eff} = \frac{D_{H^+}}{1 + \frac{C_T}{K_{eq}}}$

if $[\overline{H^+}]_0 \gg K_{eq}$; $D_{eff} = D_{H^+}$

e) $C(x,t) = C_\alpha + \hat{C}(x,t)$

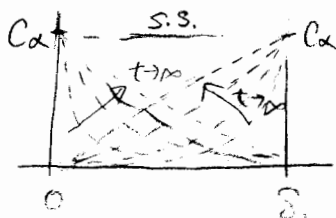
↑
Steady state
solution.

↑
Transient.

B.C. $\hat{C}(x=0, t) = 0$ } Homogeneous

$\hat{C}(x=L, t) = 0$ } B.C.

$\hat{C}(x, t=0) = -C_\alpha$ } I.C.



Note: C represents the concentration of $[\overline{H^+}]$

$$e) \hat{c}(x,t) = X(x)T(t)$$

$$\frac{\partial \hat{c}}{\partial t} = D_{\text{eff}} \frac{\partial^2 \hat{c}}{\partial x^2}$$

$$X(x) \frac{\partial T(t)}{\partial t} = T(t) \frac{\partial^2 X(x)}{\partial x^2} = -k^2$$

$$\hat{c}(x,t) = \sum_{n=1}^{\infty} A_n \sin\left(\frac{n\pi x}{L}\right) e^{-t/\tau}$$

$$\text{When } t=0, \hat{c}(x,t) = -C_\alpha$$

$$\therefore \sum_{n=1}^{\infty} A_n \sin\left(\frac{n\pi x}{L}\right) = -C_\alpha$$

$$\text{Extracting } A_n: \int_0^L \sum_{n=1}^{\infty} A_n \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi x}{L}\right) dx = \int_0^L -C_\alpha \sin\left(\frac{m\pi x}{L}\right) dx$$

$$\int_0^L A_m \sin^2\left(\frac{m\pi x}{L}\right) dx = \frac{L}{m\pi} C_\alpha \cos\left(\frac{m\pi x}{L}\right) \Big|_0^L$$

$$\int_0^L A_m \left[\frac{1}{2} - \frac{1}{2} \cos\left(\frac{2m\pi x}{L}\right) \right] dx = \frac{C_\alpha L}{m\pi} [\cos(m\pi) - 1]$$

$$\frac{L}{2} A_m$$

$$= \begin{cases} 0, & m \text{ even} \\ -\frac{2C_\alpha L}{m\pi}, & m \text{ odd} \end{cases}$$

m is a dummy variable, $A_m = A_n$

$$A_m = -\frac{4C_\alpha}{m\pi} \text{ for } m \text{ is odd}$$

$$c(x,t) = C_\alpha - \sum_{n \text{ odd}} \frac{4C_\alpha}{m\pi} \sin\left(\frac{n\pi x}{L}\right) e^{-t/\tau}$$

$$\text{B.C.: } c(x=0,t) = c(x=L,t) = C_\alpha$$

$$\text{I.C.: } c(x,t=0) = 0$$

$$\tau_{\text{diff-react}} \propto \frac{1}{D_{\text{eff}}} \propto 1 + \frac{C_T K_{\text{eq}}}{(K_{\text{eq}} + [H^+])^2}$$

$$\tau_{\text{diff}} \text{ from 2.2.1} \propto l$$

$\therefore \tau_{\text{diff-react}} > \tau_{\text{diff}}$ depending on # of binding sites.

$$\cdot T(t) = A_1 e^{-t/\tau}, \text{ where } \tau = \frac{L^2}{\pi^2 n^2 D_{\text{eff}}}$$

$$\cdot X(x) = B_1 \cos\left(\frac{n\pi x}{L}\right) + B_2 \sin\left(\frac{n\pi x}{L}\right)$$

to meet
B.C.