Singular Perturbation, Electroneutrality, and Gibbs-Donnan Equilibrium

Introduction

- Important assumptions in solving transport problems with charged species:
  - Electroneutrality
  - Gibbs-Donnan equilibrium at the membrane surface
- Prior to 1968, these had been observed experimentally but lacked an analytical basis
- In his 1968 paper[1], A. D. MacGillivray demonstrates how these assumptions may be derived

Introduction

- Electroneutrality
  - Due to strong electrical forces between charged species in solution and their high mobilities, significant separation of charge does not occur[2]
  - $\sum_i z_i C_i = 0$
- Gibbs-Donnan Equilibrium
  - A semipermeable membrane allows smaller ions to cross but not larger ones
  - Results in varying equilibrium concentrations on either side of the membrane
  - $\left(\frac{A}{\widetilde{C_A}}\right)^{z_A} = \left(\frac{B}{\widetilde{C_B}}\right)^{z_B} = e^{-D}$

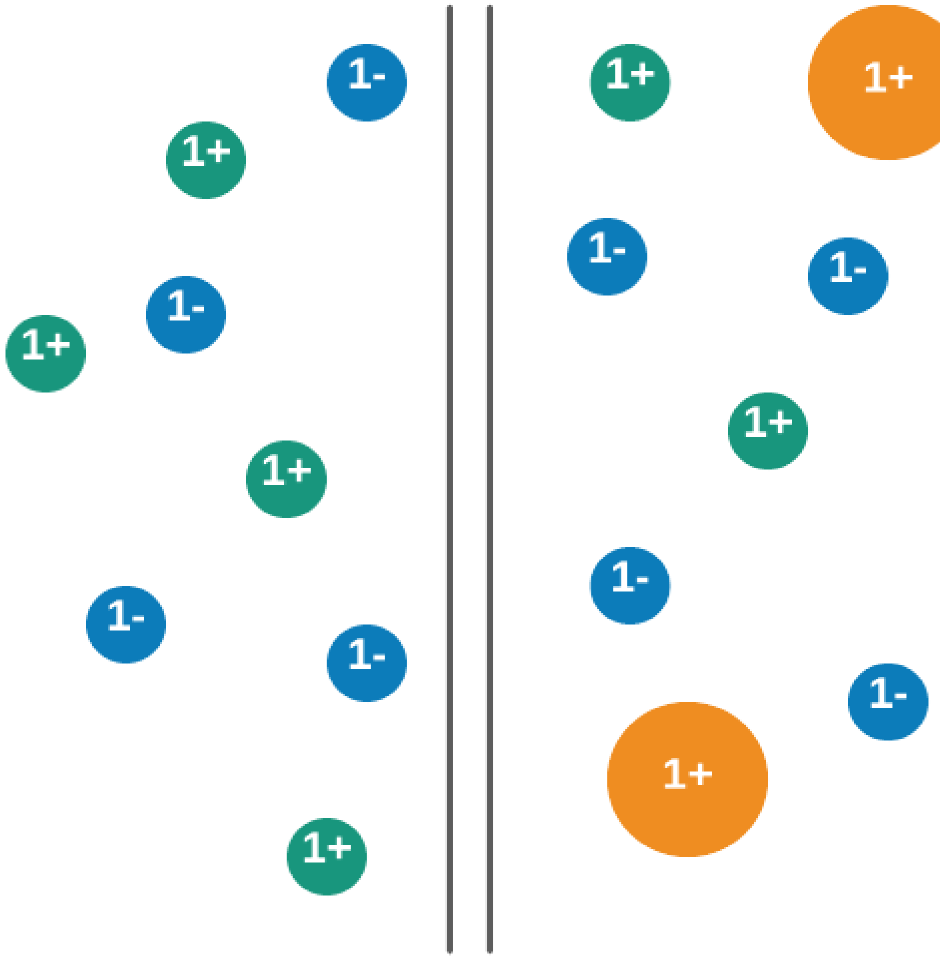


Figure 1: Example of a system obeying both electroneutrality and Gibbs-Donnan Equilibrium

Methods – Governing Equations

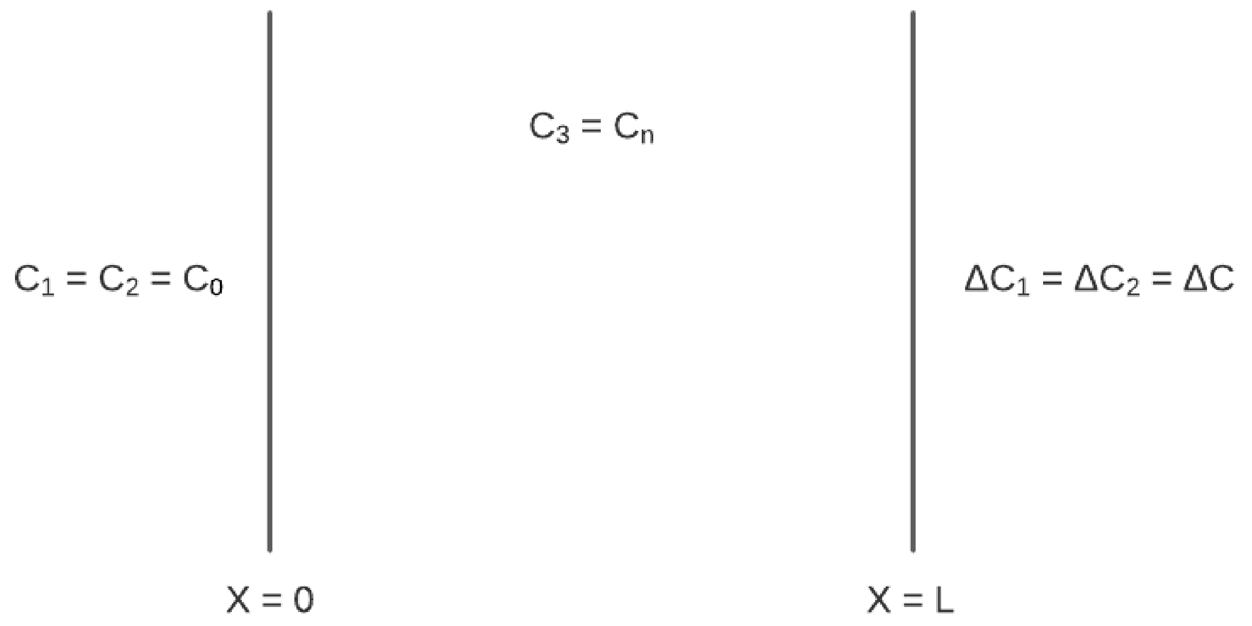
- Nernst-Planck Equation:
  - $N_i = C_i v - D_i \left(\nabla C_i + \frac{z_i F}{RT} C_i \nabla \phi \right)$
  - Notice the addition of a migration term to our typical transport equation
  - An additional equation is needed to solve for the potential gradient
- Poisson's Equation:
  - $\nabla^2 \phi = -\frac{F}{\xi} \sum_i z_i C_i$

Methods – Singular Perturbation

- Similar to regular perturbation but when ϵ becomes large in certain limits of the system (for example close to the walls)
- May be identified by when setting $\epsilon = 0$ reduces the order of the differential equation
- I will demonstrate singular perturbation by deriving Gibbs-Donnan equilibrium in my results section

Problem Set Up

- The problem we will be considering is the transport of ions through a charged membrane
- $z_1 = +1$
- $z_2 = -1$
- $z_3 = +1$
- No convection



Results and Discussion – Electroneutrality Derivation

- Poisson's Equation:
  - $\nabla^2 \phi = -\frac{F}{\xi} \sum_i z_i C_i$
- Non-dimensionalized version:
  - $\epsilon^2 \frac{d^2 \tilde{\phi}}{d\tilde{x}} = -[\tilde{C}_1 - \tilde{C}_2 + \tilde{C}_n]$
  - where $\epsilon^2 = \frac{RT\xi}{F^2 L^2 \Delta C}$
- We get the electroneutrality equation if $\epsilon \rightarrow 0$:
  - 0= $\tilde{C}_1 - \tilde{C}_2 + \tilde{C}_n$
  - $\sum_i z_i C_i = 0$

Results and Discussion – Electroneutrality Derivation

- When is the assumption of electroneutrality valid?
  - $\epsilon \to 0$
  - $\epsilon^2 = \frac{RT\xi}{F^2 L^2 \Delta C}$
- When L is large compared to the Debye length
  - Analogous to the thickness of the boundary layer for potential
- Or when ΔC is small compared to C_0
  - $\epsilon^2 \frac{d^2\tilde{\phi}}{d\tilde{x}} = -[\tilde{C}_1 - \tilde{C}_2 + \tilde{C}_n]$
  - $\tilde{C}_i = \frac{C_i}{\Delta C}$

Results and Discussion – Gibbs-Donnan Equilibrium

- Non-dimensionalized Nernst-Planck and Poisson equations:
  - $\tilde{N}_1 = -\tilde{C}_1 \frac{d\tilde{\Phi}}{d\tilde{x}} - \frac{d\tilde{C}_1}{d\tilde{x}}$
  - $\tilde{N}_2 = \tilde{C}_2 \frac{d\tilde{\Phi}}{d\tilde{x}} - \frac{d\tilde{C}_2}{d\tilde{x}}$
  - $\epsilon^2 \frac{d^2\tilde{\Phi}}{d\tilde{x}} = -[\tilde{C}_1 - \tilde{C}_2 + \tilde{C}_n]$
- Since ϵ is often small, this suggests using a perturbation scheme to solve.
- Zeroth-order in ϵ:
  - $0 = -\left[\tilde{C}_1^{(0)} - \tilde{C}_2^{(0)} + \tilde{C}_n\right]$
  - Need to use singular perturbation

Singular Perturbation Steps

- Steps to solve:
  1. Use regular perturbation to solve for the solution in the bulk (the outer solution)
  2. Use a change of variables to make the small term ~ 1 when $\epsilon \rightarrow 0$, then solve for the solution close to the wall via perturbation (inner solution)
  3. Match the two solutions via asymptotic matching

Using Singular Perturbation to Derive Gibbs-Donnan Equilibrium

1. Use regular perturbation to solve for the solution in the bulk (the outer solution)
   - Solving ODE's like we have done before
   - We will skip this part and assume a solution exists and that the limits of that solution are as follows:
     - $\lim_{\tilde{x}\to 0} \tilde{C}_1^{(0)}(\tilde{x}) = A$
     - $\lim_{\tilde{x}\to 0} \tilde{C}_2^{(0)}(\tilde{x}) = B$
     - $\lim_{\tilde{x}\to 0} \tilde{\Phi}(\tilde{x}) = D$

Using Singular Perturbation to Derive Gibbs-Donnan Equilibrium

2. Use a change of variables to make the small term ~1 when $\epsilon \to 0$, then solve for the solution close to the wall via perturbation (inner solution)

- $\epsilon^2 \frac{d^2\tilde{\phi}}{d\tilde{x}} = -[\tilde{C}_1 - \tilde{C}_2 + \tilde{C}_n]$
- Let $x_\eta = \frac{\tilde{x}}{\epsilon}$
- Solving for zeroth order in ϵ:
  - $0 = -\hat{C}_1^{(0)} \frac{d\widehat{\Phi}^{(0)}}{x_\eta} - \frac{d\hat{C}_1^{(0)}}{x_\eta}$
  - $0 = \hat{C}_2^{(0)} \frac{d\widehat{\phi}^{(0)}}{x_\eta} - \frac{d\hat{C}_2^{(0)}}{x_\eta}$
  - $\frac{d^2\widehat{\phi}^{(0)}}{dx_\eta^2} = -\left[\hat{C}_1^{(0)} - \hat{C}_2^{(0)} + \tilde{C}_n\right]$
- Solution:
  - $\hat{C}_1^{(0)}(x_\eta) = \tilde{C}_0 e^{-\widehat{\Phi}^{(0)}(x_\eta)}, \qquad \hat{C}_2^{(0)}(x_\eta) = \tilde{C}_0 e^{\widehat{\Phi}^{(0)}(x_\eta)}$

Using Singular Perturbation to Derive Gibbs-Donnan Equilibrium

3. Match the two solutions via asymptotic matching
   - The limit of the outer solution as $\tilde{x}$ approaches zero must equal the limit of the inner solution as x_η approaches infinity
   - Solution:
     - $A = \tilde{C}_0 e^{-\hat{\Phi}^{(0)}(\infty)}$
     - $B = \tilde{C}_0 e^{\hat{\Phi}^{(0)}(\infty)}$
     - $\hat{\phi}^{(0)}(\infty) = D$
   - Rearranged this gives us:
     - $\left(\frac{A}{\widetilde{C_A}}\right)^{z_A} = \left(\frac{B}{\widetilde{C_B}}\right)^{z_B} = e^{-D}$

Summary

- MacGillivray's 1968 publication provides a sound analytical argument for the validity of the electroneutrality and Gibbs-Donnan equilibrium assumptions
- These derivations may be applied on a much larger scale
- Gibbs-Donnan equilibrium is valid in any system involving a membrane that obeys the Nernst-Planck and Poisson equations
- Electroneutrality is valid when the length scale of the system is large and the concentration gradient is small
- Understanding where these assumptions come from gives insight into their limits

References

1. A. D. MacGillivray, "Nernst-Planck Equations and the Electroneutrality and Donnan Equilibrium Assumptions," *The Journal of Chemical Physics,* vol. 48, no. 7, pp. 2903-2906, 1968.
2. T. F. Fuller and J. N. Harb, Electrochemical Engineering, John Wiley & Sons, Incorporated, 2018.