

Biophysics I (BPHS 3090)

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Website: <http://www.yorku.ca/cberge/3090W2015.html>

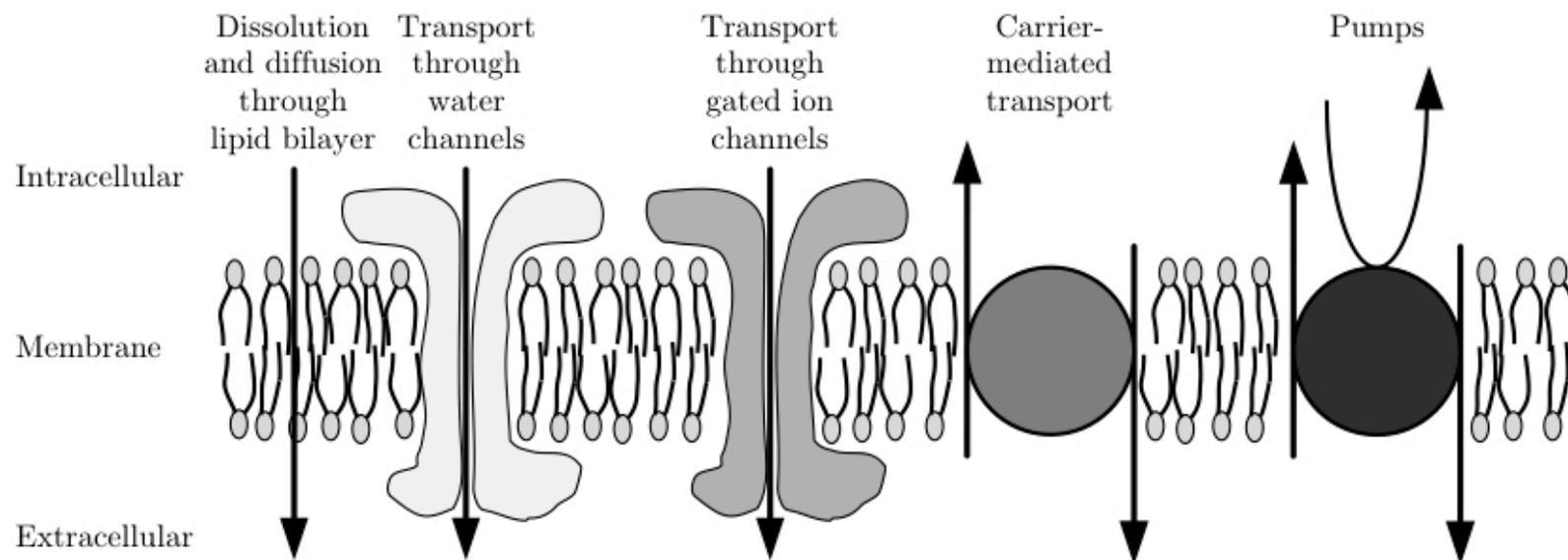
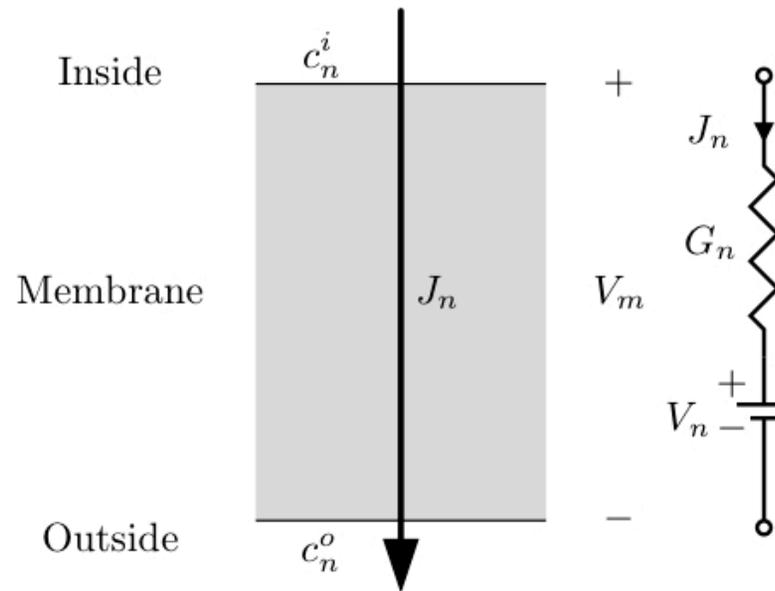


Figure 2.19

Model of Steady-State Electrodiffusion through Membranes



→ Now we will consider the effect of solutes having charge

Equations of Electrodiffusion

Nernst-Planck Equation

$$J_n(x, t) = -z_n F D_n \frac{\partial c_n(x, t)}{\partial x} - u_n z_n^2 F^2 c_n(x, t) \frac{\partial \psi(x, t)}{\partial x}$$

Continuity

$$\frac{\partial J_n(x, t)}{\partial x} = -z_n F \frac{\partial c_n(x, t)}{\partial t}$$

Poisson's Equation

$$\frac{\partial^2 \psi(x, t)}{\partial x^2} = -\frac{1}{\epsilon} \sum_n z_n F c_n(x, t)$$

Some new variables

z_n - charge # (or “valence charge”)
(e.g., +1, -1, +2, 0, etc...) [re $1 e = 1.602 \times 10^{-12} \text{ C}$]

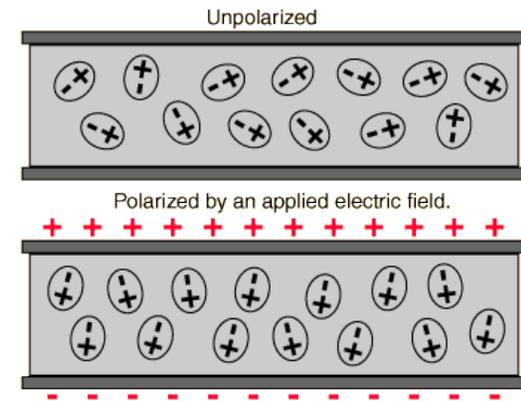
F - Faraday's constant [$9.65 \times 10^4 \text{ C/mol}$]

J_n - current density [A/cm^2]

ψ - electrical potential [V]

ϵ - permittivity [F/m]

u_n - mechanical mobility [s/kg]



<http://en.wikipedia.org/wiki/Permittivity>

from Einstein
relation

Mobility & Stokes-Einstein Relation

u_n - mechanical mobility [s/kg] from Einstein relation

➤ Force (f_p) required to move a sphere of radius a through a viscous medium of viscosity η with a velocity of v is

$$f_p = 6\pi a\eta v$$

Stoke's Law
(eqn.3.22)

➤ Particle mobility, u_p , is defined as the ratio of the particle velocity to the force on the particle

$$u_p \equiv \frac{v}{f_p} = \frac{1}{6\pi a\eta}$$

Similar to
(reciprocal of)
impedance

➤ Relating to the diffusion constant (Annus Mirabilis):

$$D = u_p kT = u N_A kT = uRT$$

$$D_n = u_n RT$$

1. u_n is the molar mechanical mobility of ion n . In some fields (e.g., solid-state physics), it is customary to use the *molar electrical mobility*, \hat{u}_n , where $\hat{u}_n = |z_n|F u_n$. \hat{u}_n has units of (cm/s)/(V/cm). In terms of the molar electrical mobility, the Einstein relation is $D_n = (RT\hat{u}_n)/(|z_n|F)$.

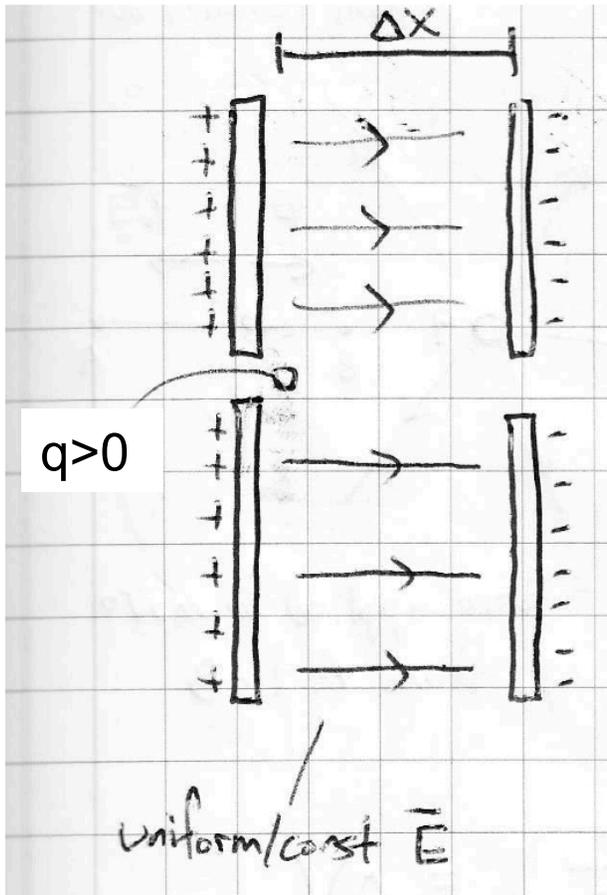
Nernst-Planck Equation → Electrodiffusion

current
density

$$J_n(x, t) = \underbrace{-z_n F D_n \frac{\partial c_n(x, t)}{\partial x}}_{\text{diffusion}} - \underbrace{u_n z_n^2 F^2 c_n(x, t) \frac{\partial \psi(x, t)}{\partial x}}_{\text{electric drift}}$$

→ Essentially a charged version of Fick's first law, but now with an additional term due to electric forces (the *drift* term on the right)

Electric Drift



→ Consider a charge q placed between two uniformly/oppositely charged plates

- uniform E field between
- force exerted on charge (Coulomb's law)

$$\mathbf{F} = q\mathbf{E}$$

- E depends upon spatial gradient of the potential

$$E = -\frac{\partial\psi}{\partial x}$$

Think in terms of energy (e.g., where does it com from? conserved?)

$$J_n(x, t) = -z_n F D_n \frac{\partial c_n(x, t)}{\partial x} - u_n z_n^2 F^2 c_n(x, t) \frac{\partial \psi(x, t)}{\partial x}$$

Continuity Equation

$$\frac{\partial J_n(x, t)}{\partial x} = -z_n F \frac{\partial c_n(x, t)}{\partial t}$$

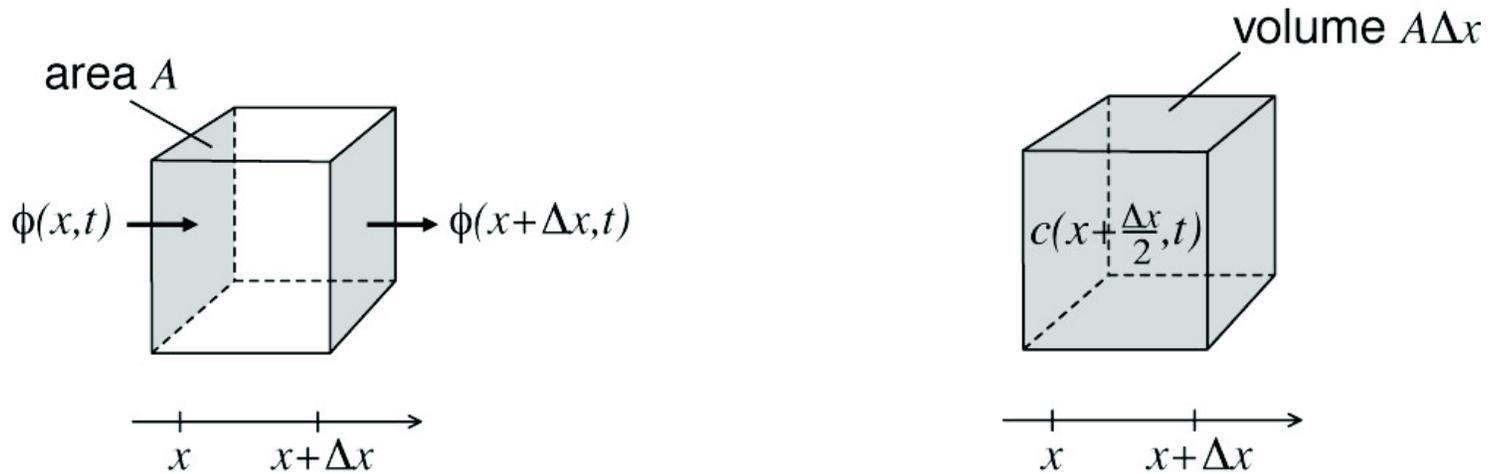
spatial change in
current density

temporal change in
charge density

→ Just like our derivation for diffusion, this essentially tells us about the conservation of charge

Review: Continuity Equation (re diffusion)

⇒ imagine a cube (with face area A and length Δx) and a time interval Δt



solute entering from left - solute exiting from right
(during time interval $[t, t+\Delta t]$)

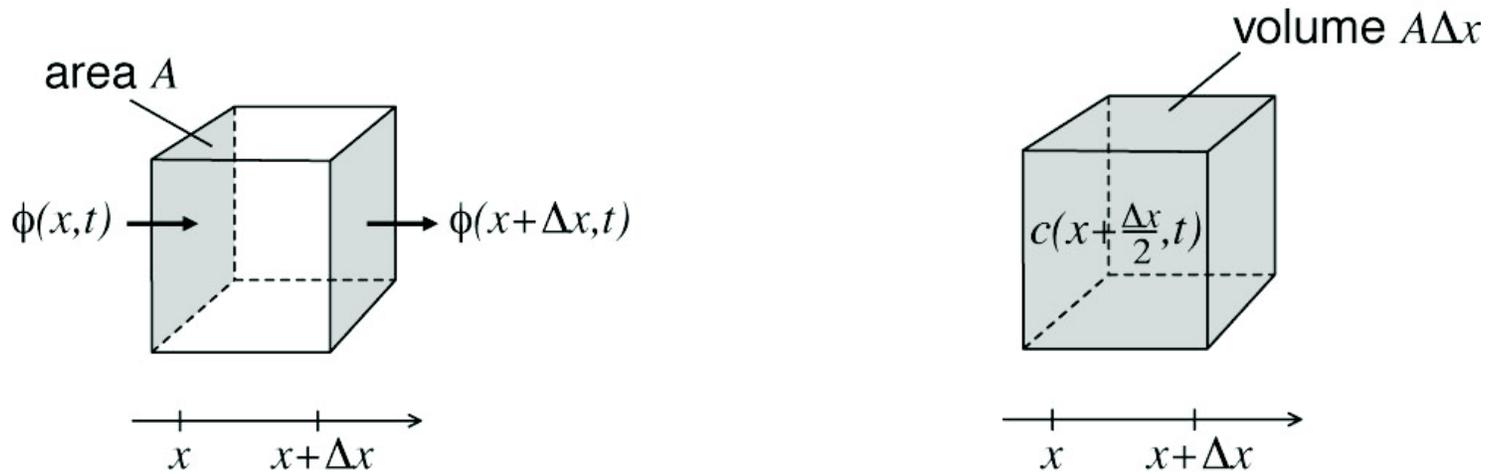
=

change in amount of solute inside cube
(during time interval $[t, t+\Delta t]$)

$$A \Delta t \phi(x, t)$$

$$A \Delta x c(x, t)$$

Review: Continuity Equation (re diffusion)



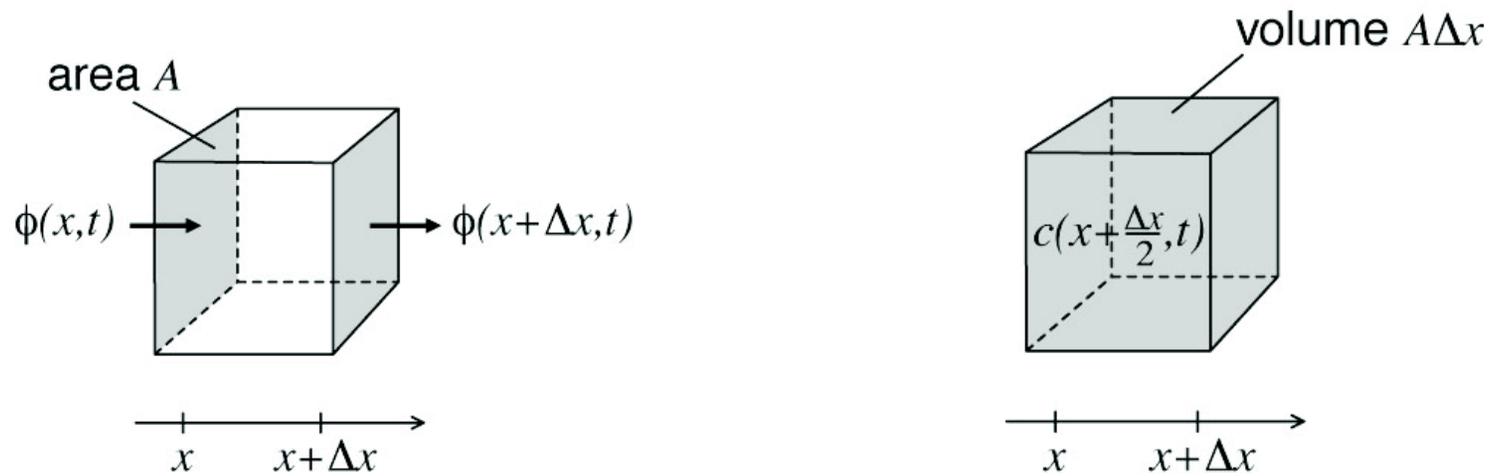
solute entering from left - solute exiting from right
(during time interval $[t, t+\Delta t]$) = change in amount of solute inside cube
(during time interval $[t, t+\Delta t]$)

$$A \Delta t \phi(x, t + \Delta t/2) - A \Delta t \phi(x + \Delta x, t + \Delta t/2) = A \Delta x c(x + \Delta x/2, t + \Delta t) - A \Delta x c(x + \Delta x/2, t)$$

$$\frac{\phi(x + \Delta x, t + \Delta t/2) - \phi(x, t + \Delta t/2)}{\Delta x} = \frac{c(x + \Delta x/2, t + \Delta t) - c(x + \Delta x/2, t)}{\Delta t}$$

$$\implies \frac{\partial \phi}{\partial x} = - \frac{\partial c}{\partial t}$$

Review: Continuity Equation



$$\implies \frac{\partial \phi}{\partial x} = -\frac{\partial c}{\partial t}$$

$$\frac{\partial J_n(x,t)}{\partial x} = -z_n F \frac{\partial c_n(x,t)}{\partial t}$$

Relationship between current density and flux:

$$J_n(x,t) = z_n F \phi_n(x,t)$$

Poisson's Equation

$$\frac{\partial^2 \psi(x, t)}{\partial x^2} = -\frac{1}{\epsilon} \sum_n z_n F c_n(x, t)$$

→ Stemming from Gauss' Law, relates the charge density and electric potential

charge density [C/m³]

$$\rho = \sum_n z_n F c_n(x, t)$$

Electrostatics [edit]

Main article: [Electrostatics](#)

One of the cornerstones of [electrostatics](#) is setting up and solving problems described by the Poisson equation. Solving the Poisson equation amounts to finding the [electric potential](#) ϕ for a given [charge](#) distribution ρ_f .

The mathematical details behind Poisson's equation in electrostatics are as follows ([SI units](#) are used rather than [Gaussian units](#), which are also frequently used in [electromagnetism](#)).

Starting with [Gauss's law](#) for electricity (also one of [Maxwell's equations](#)) in differential form, we have:

$$\nabla \cdot \mathbf{D} = \rho_f$$

where $\nabla \cdot$ is the [divergence operator](#), \mathbf{D} = [electric displacement field](#), and ρ_f = [free charge density](#) (describing charges brought from outside). Assuming the medium is linear, isotropic, and homogeneous (see [polarization density](#)), we have the [constitutive equation](#):

$$\mathbf{D} = \epsilon \mathbf{E}$$

where ϵ = [permittivity](#) of the medium and \mathbf{E} = [electric field](#). Substituting this into Gauss's law and assuming ϵ is spatially constant in the region of interest obtains:

$$\nabla \cdot \mathbf{E} = \frac{\rho_f}{\epsilon}$$

In the absence of a changing magnetic field, \mathbf{B} , [Faraday's law of induction](#) gives:

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} = 0$$

where $\nabla \times$ is the [curl operator](#) and t is time. Since the [curl](#) of the electric field is zero, it is defined by a scalar electric potential field, φ (see [Helmholtz decomposition](#)).

$$\mathbf{E} = -\nabla \varphi$$

The derivation of Poisson's equation under these circumstances is straightforward. Substituting the potential gradient for the electric field

$$\nabla \cdot \mathbf{E} = \nabla \cdot (-\nabla \varphi) = -\nabla^2 \varphi = \frac{\rho_f}{\epsilon},$$

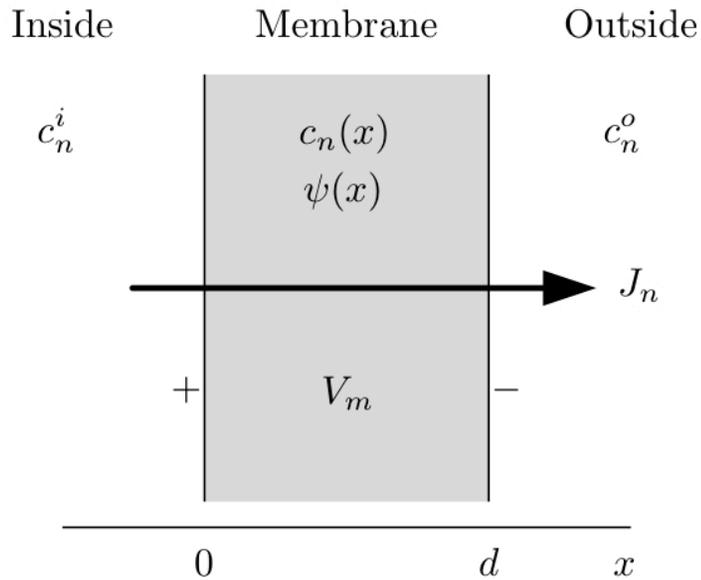
directly obtains **Poisson's equation** for electrostatics, which is:

$$\nabla^2 \varphi = -\frac{\rho_f}{\epsilon}.$$

Solving Poisson's equation for the potential requires knowing the charge density distribution. If the charge density is zero, then [Laplace's equation](#) results. If the charge density follows a [Boltzmann distribution](#), then the [Poisson-Boltzmann equation](#) results. The Poisson–Boltzmann equation plays a role in the development of the [Debye–Hückel theory of dilute electrolyte solutions](#).

The above discussion assumes that the magnetic field is not varying in time. The same Poisson equation arises even if it does vary in time, as long as the [Coulomb gauge](#) is used. In this more general context, computing ϕ is no longer sufficient to calculate \mathbf{E} , since \mathbf{E} also depends on the [magnetic vector potential](#) \mathbf{A} , which must be independently computed. See [Maxwell's equation in potential formulation](#) for more on ϕ and \mathbf{A} in Maxwell's equations and how Poisson's equation is obtained in this case.

Steady-State Electrodiffusion through Membranes



Steady-state

$$\rightarrow \frac{\partial c_n(x, t)}{\partial t} = 0$$

$$\rightarrow \frac{\partial J_n(x, t)}{\partial x} = 0$$

$$\rightarrow J_n = \text{constant}$$

Electrolyte solutions \rightarrow Electroneutrality

$$\text{if } t \gg \tau_r \text{ and } x \gg \Lambda_D \text{ then } \sum_n z_n F c_n(x, t) = 0$$

$$\frac{\partial^2 \psi(x, t)}{\partial x^2} = -\frac{1}{\epsilon} \sum_n z_n F c_n(x, t)$$

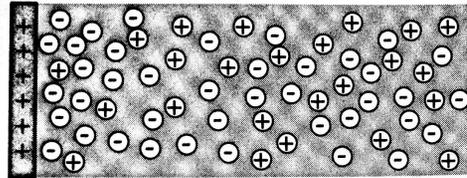
\rightarrow Simplifies Poisson's equation such that ψ is a linear function across the membrane

Electrolyte solutions → Electroneutrality

if $t \gg \tau_r$ and $x \gg \Lambda_D$ then $\sum_n z_n F c_n(x, t) = 0$

- Charge Relaxation Time τ_r

Measures temporal change in charge density
(i.e., relaxation time of charge distribution)



- Debye Length Λ_D

Measures spatial extent of electric potential
(i.e., distance over which electroneutrality is violated)

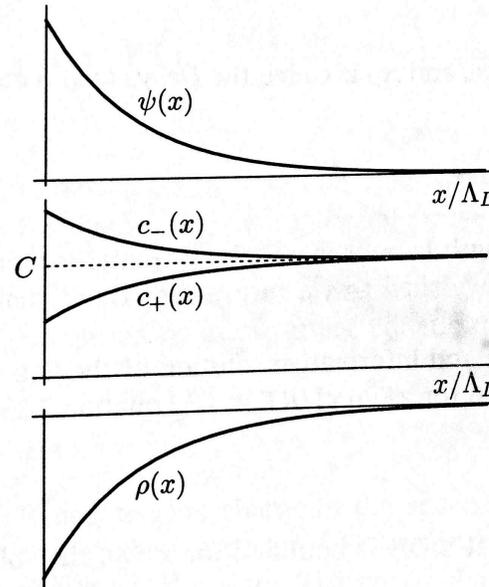
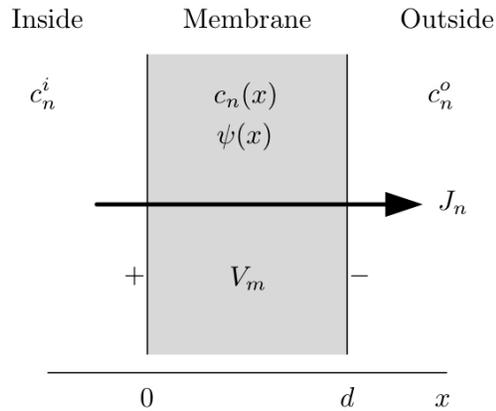


Figure 7.7 The spatial distribution of charge near a plate containing positive fixed charges. The counterions are anions and are in higher concentration near the plate than far from the plate. The cations are at a lower concentration near the plate than far from the plate. The spatial distributions of both mobile ions are exponential, with space constant equal to the Debye length.

→ Both are very small (1 ns and 1 nm respectively; see Weiss v.1 7.2.3), justifying that ionic solutions obey electroneutrality

Steady-State Electrodiffusion through Membranes



Steady-state

$$\begin{aligned} \rightarrow \frac{\partial c_n(x, t)}{\partial t} &= 0 \\ \rightarrow \frac{\partial J_n(x, t)}{\partial x} &= 0 \\ \rightarrow J_n &= \text{constant} \end{aligned}$$

Rearrange Nernst-Planck Equation

$$J_n = -z_n F D_n \frac{dc_n(x)}{dx} - u_n z_n^2 F^2 c_n(x) \frac{d\psi(x)}{dx} = -u_n z_n^2 F^2 c_n(x) \left[\frac{D_n}{u_n z_n F c_n(x)} \frac{dc_n(x)}{dx} + \frac{d\psi(x)}{dx} \right]$$

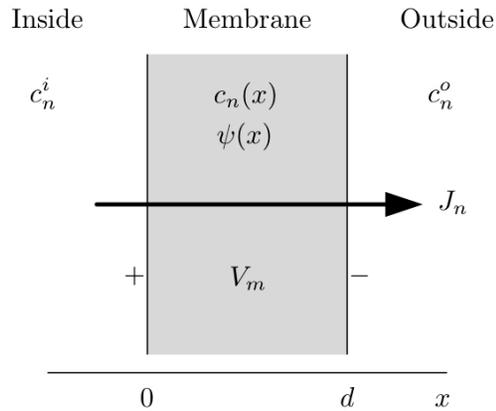
Integrate across membrane

$$J_n \int_0^d \underbrace{\frac{dx}{u_n z_n^2 F^2 c_n(x)}}_{\frac{1}{G_n}} = - \int_0^d \frac{d}{dx} \left[\frac{RT}{z_n F} \ln c_n(x) + \psi(x) \right] dx$$

Rearrange/Rename

$$J_n \frac{1}{G_n} = - \overbrace{\frac{RT}{z_n F} \ln \frac{c_n(d)}{c_n(0)}}^{V_n} + \overbrace{\psi(0) - \psi(d)}^{V_m} \rightarrow \boxed{J_n = G_n (V_m - V_n)}$$

Steady-State Electrodiffusion through Membranes



Steady-state

$$\rightarrow \frac{\partial c_n(x, t)}{\partial t} = 0$$

$$\rightarrow \frac{\partial J_n(x, t)}{\partial x} = 0$$

$$\rightarrow J_n = \text{constant}$$

$$J_n = G_n(V_m - V_n)$$

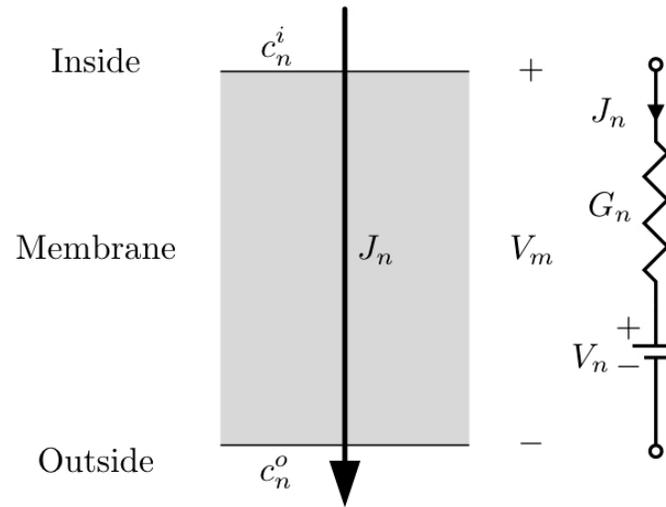
Nernst Equilibrium Potential

$$V_n = \frac{RT}{z_n F} \ln \frac{c_n(d)}{c_n(0)} = \frac{RT}{z_n F} \ln \frac{c_n^o}{c_n^i}$$

→ Like Ohm's law!

$$G_n = \frac{1}{\int_0^d \frac{dx}{u_n z_n^2 F^2 c_n(x)}} \geq 0$$

Model of Steady-State Electrodiffusion through Membranes



Nernst Equilibrium Potential $V_n = \frac{RT}{z_n F} \ln \frac{c_n^o}{c_n^i}$

Electrical Conductivity $G_n = \frac{1}{\int_0^d \frac{dx}{u_n z_n^2 F^2 c_n(x)}} \geq 0$