Biophysics I (BPHS 4080)

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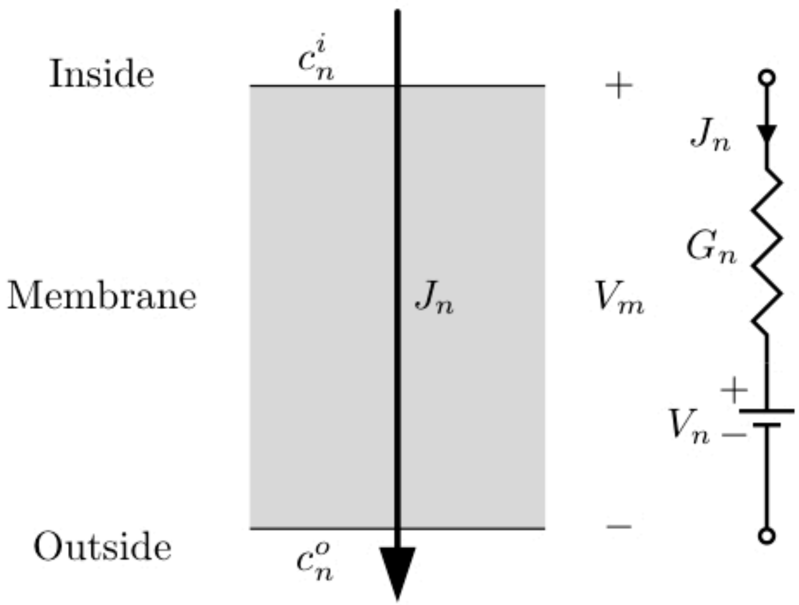
Lecture 12

Reference/Acknowledgement:
- TF Weiss (Cellular Biophysics)
- D Freeman

Model of Steady-State Electrodiffusion through Membranes



→ Now we will consider the effect of solutes having charge

Equations of Electrodiffusion

Nernst-Plank 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

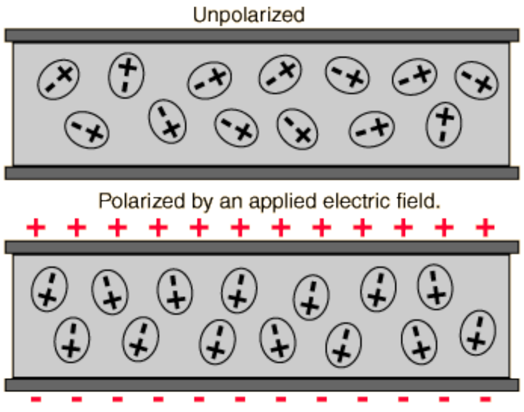
z_n - charge # (or "valence charge")
(e.g., +1, -1, +2, 0, etc...) [re $1\ e = 1.602 \times 10^{-19}$ C]

F - Faraday's constant [9.65×10^4 C/mol]

J_n - current density [A/cm^2]

ψ - electrical potential [V]

ϵ - permittivity [F/m]



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

u_n - mechanical mobility [s/kg]

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 ν is

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

Stoke's Law (eqn.3.22)

- Particle mobility, υ_p, is defined as the ratio of the particle velocity to the force on the particle

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

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-Plank Equation → Electrodiffusion

current density

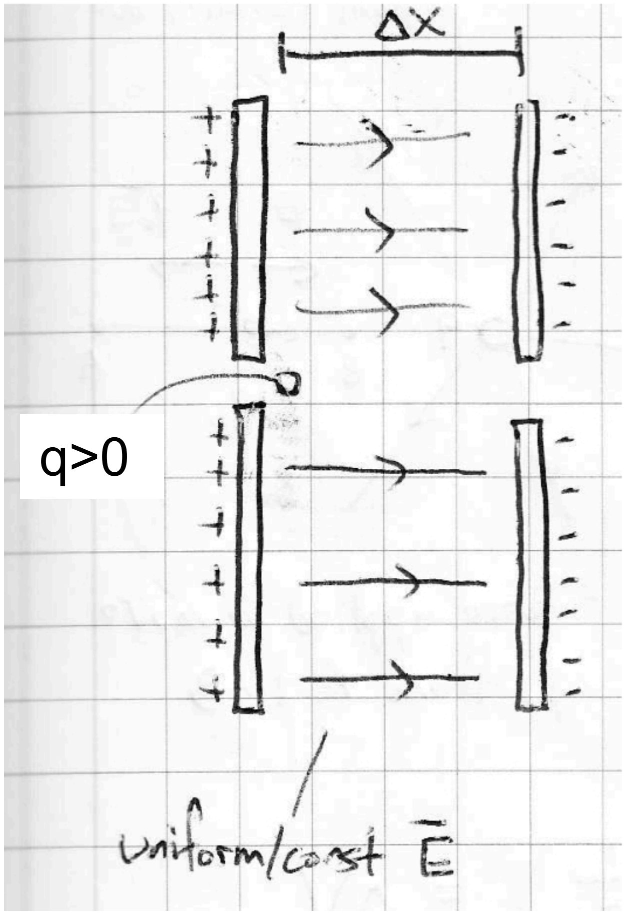
$$J_n(x,t) = -z_n F D_n \frac{\partial c_n(x,t)}{\partial x} - u_n z_n^2 F^2 c_n(x,t) \frac{\partial \psi(x,t)}{\partial x}$$

diffusion

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

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

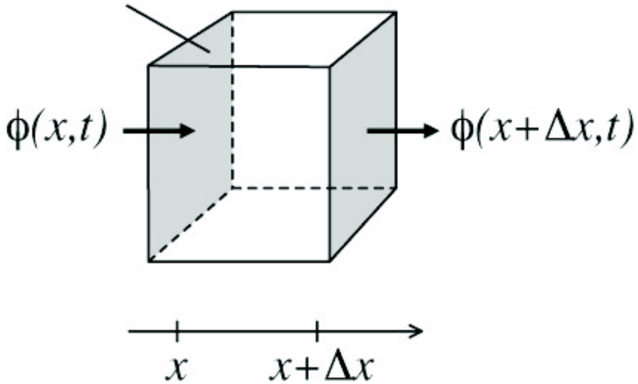
spatial change in current density

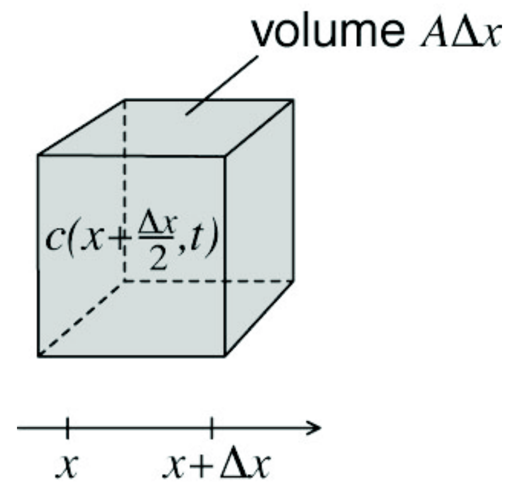
temporal change in charge density

→ 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

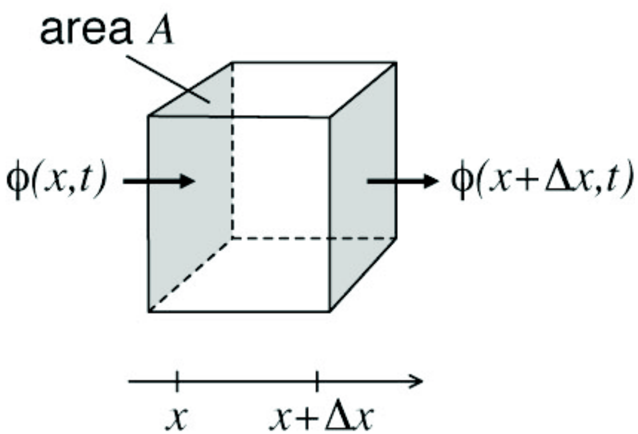


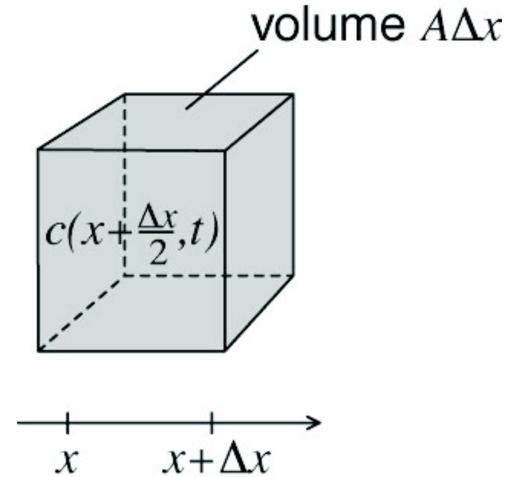


solute entering from *left* - solute exiting from *right* = change in amount of solute *inside* cube
(during time interval $[t, t+\Delta t]$) (during time interval $[t, t+\Delta t]$)

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

Review: Continuity Equation (re diffusion)





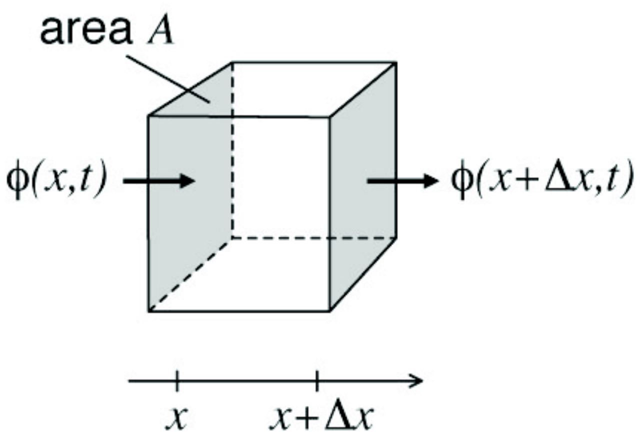
solute entering from left - solute exiting from right (during time interval [t, $t+\Delta t$]) = change in amount of solute inside cube (during time interval [t, $t+\Delta t$])

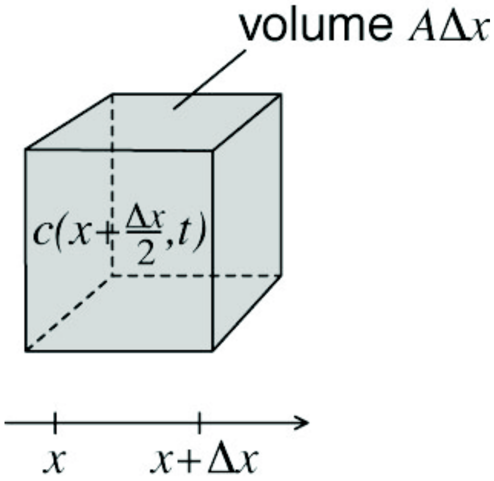
$$A\,\Delta t\,\phi(x,t+\Delta t/2) - A\,\Delta t\,\phi(x+\Delta x,t+\Delta t/2) = A\,\Delta x\,c(x+\Delta x/2,t+\Delta t) - A\,\Delta x\,c(x+\Delta x/2,t)$$

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

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

Review: Continuity Equation





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

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

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/m^3]

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

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, **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:

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

where ε = permittivity of the medium and **E** = electric field. Substituting this into Gauss's law and assuming ε is spatially constant in the region of interest obtains:

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

In the absence of a changing magnetic field, **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

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

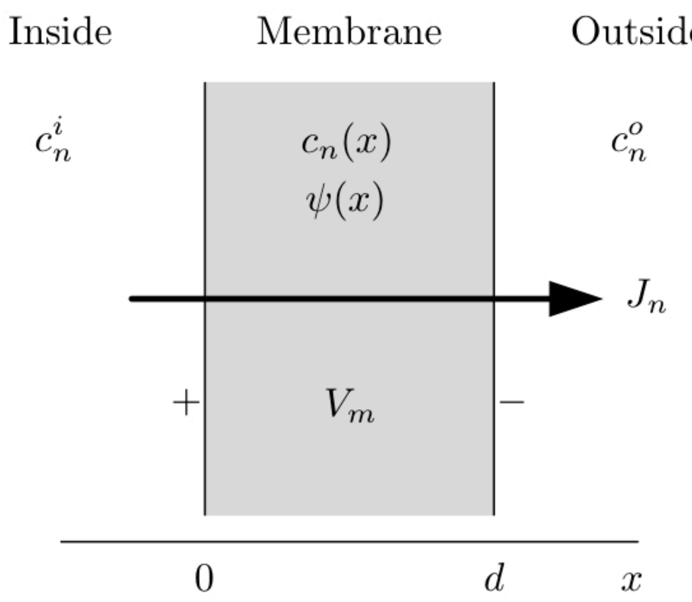
directly obtains **Poisson's equation** for electrostatics, which is:

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

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 **E**, since **E** also depends on the magnetic vector potential **A**, which must be independently computed. See Maxwell's equation in potential formulation for more on ϕ and **A** in Maxwell's equations and how Poisson's equation is obtained in this case.

Steady-State Electrodiffusion through Membranes



Steady-state

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

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

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

Electrolyte solutions → Electroneutrality

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

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

→ Simplifies Poisson’s equation such that ψ is a linear function across the membrane

Electrolyte solutions → Electroneutrality

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

- 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)

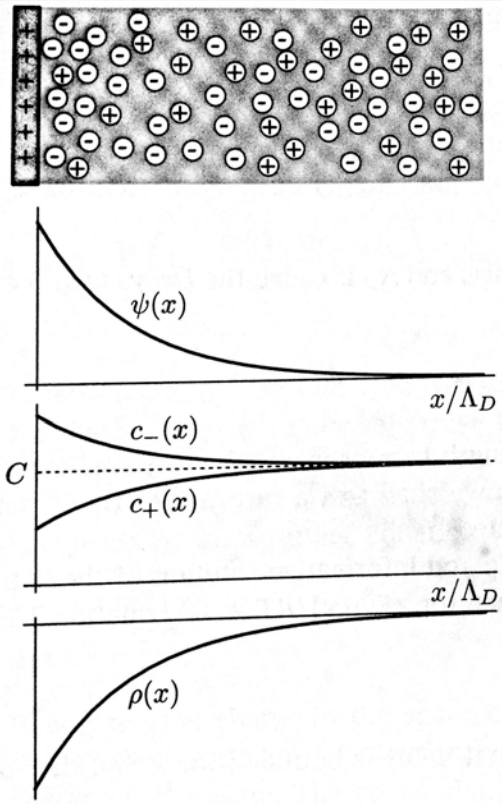
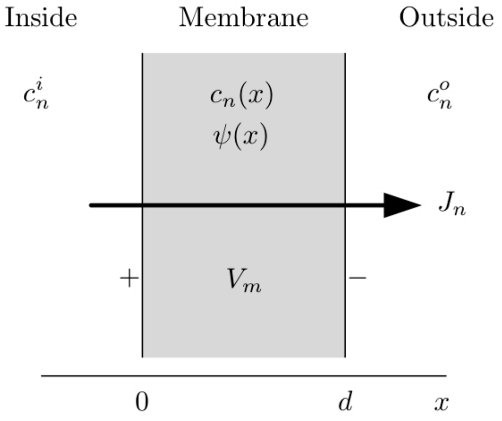


Figure 7.7 The spatial distribution of charge near a plate containing positive fixed charges. The counterions are anions and are in higher concentration near the plate than far from the plate. The cations are at a lower concentration near the plate than far from the plate. The spatial distributions of 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

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

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

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

Rearrange Nernst-Plank 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

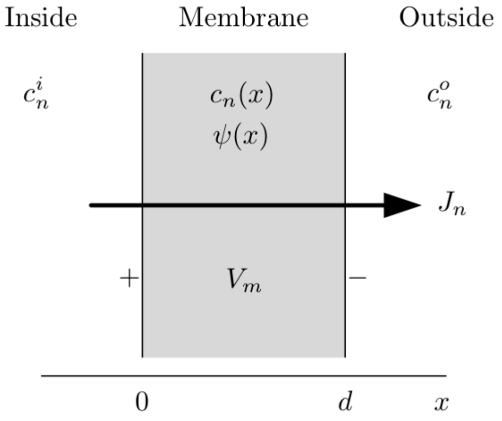
$$J_n \underbrace{\int_0^d \frac{dx}{u_n z_n^2 F^2 c_n(x)}}_{\frac{1}{G_n}} = -\int_0^d \frac{d}{dx} \left[\frac{RT}{z_n F} \ln c_n(x) + \psi(x) \right] dx$$

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

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

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

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

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

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

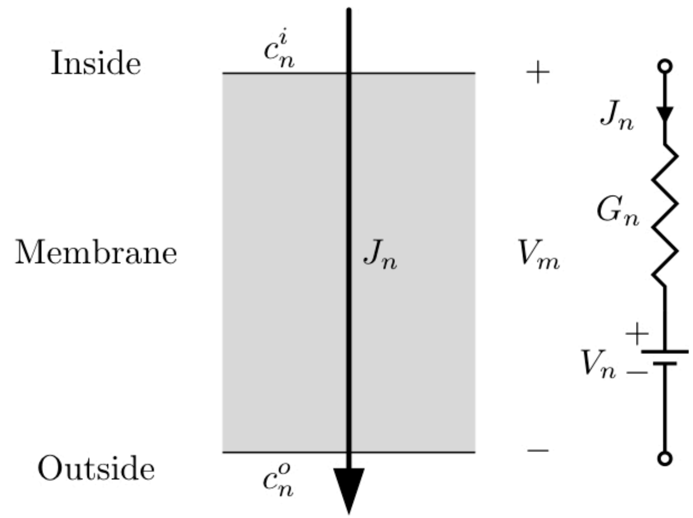
→ Like Ohm's law!

Nernst Equilibrium Potential

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

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

Model of Steady-State Electrodiffusion through Membranes



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

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