Lecture 34

Last Time: transport laws

① $\mu \rightarrow \mu_g(x)$ (assumptions valid only if $\mu_g(x)$ varies smoothly w/ x)

② $J = -uc \dfrac{d\mu_g}{dx}$ (proved using stat mech) $u = \dfrac{1}{\gamma}$

Also: $\dfrac{\partial J}{\partial x} = \dfrac{-\partial c}{\partial t}$ $\nabla \cdot J > 0$, $\dfrac{\partial c}{\partial t} < 0$ (or $J = 0$, steady state)

examples: $\dfrac{\partial c}{\partial t} = D \dfrac{\partial^2 c}{\partial x^2}$ for simple solute (fick's "law")

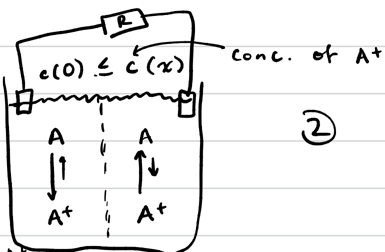
$c(x) = c(0)\, e^{\overbrace{-\Delta\mu/RT}^{\text{boltzmann factor}}}$ for Mg^{++} (or any substrate)

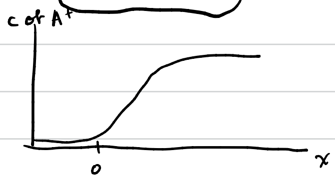
$v_{drift} = \dfrac{\varepsilon \cdot z}{\gamma}$ (gel electrophoresis)

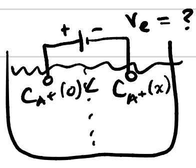
$I = \dfrac{V_e}{R}$ $R = \dfrac{LRT}{z^2 D A c}$ $D = uRT$

Today: more "laws"

ex: Nernst Equation for rxn held in steady state by an opposing potential; half rxn







① $\mu_{gA^+}(x) = \mu^{(0)}_{A^+} + RT \ln c_{A^+}(x) + z_{A^+} V_e$

② $\dfrac{d\mu_{gA^+}}{dx} = 0 + RT \dfrac{d \log c_{A^+}(x)}{dx} + z_{A^+} \dfrac{dV_e}{dx}$

$\Rightarrow$ Flux $= J = u \cdot c \cdot \left(RT \dfrac{d \log c_{A^+}(x)}{dx} + z_{A^+} \dfrac{dV_e}{dx} \right)$

In steady state $J = 0$

$$\frac{dV_e}{dx} = \frac{-RT}{z_{A^+}} \frac{d \log c_{A^+}(x)}{dx}$$

$$\int_0^x dx \frac{dV_e}{dx} = \frac{-RT}{z_{A^+}} \int_0^x dx \frac{d \ln c_{A^+}(x)}{dx}$$

$$V_e \Big|_0^x = \frac{-RT}{z_{A^+}} \ln c_{A^+}(x) \Big|_0^x$$

$$V_e(x) - V_e(0) = \frac{-RT}{z_{A^+}} \left(\ln c_{A^+}(x) - \ln c_{A^+}(0) \right)$$

$$\Delta V_e = \frac{-RT}{q_{A+} \cdot F} \ln\left(\frac{c_{A+}(x)}{c_{A+}(0)} \right)$$

"Nernst equation"

integer

coulounbs / mol