

Lecture 33 review: Deriving transport equ.

1. Find  $\mu_i(x)$ :  $WCE - SCE \rightarrow E(s) \rightarrow GCT \rightarrow \mu_i(T) = \frac{\partial G}{\partial n_i}$   
 $\mu_i(T, x)$

ex: 1.  $\mu_i = \mu_i^{(0)} + RT \ln [c_i(x)]$   
 (Ideal solution, 1 solute)

2a: Calculate flux:  $(\text{mol} \cdot \text{m}^{-2} \cdot \text{s})$   
 $J_i = -c_i v_i = -D_i \frac{dc_i}{dx} \left( \gamma = \frac{1}{U} = \frac{RT}{D} \right)$

2a:  $J = -D \frac{dc}{dx}$   
 2b:  $J = -D \frac{d^2c}{dx^2}$  (Fick's Law)

2b: Use continuity equation:

$\frac{\partial c_i}{\partial t} = -\frac{\partial J_i}{\partial x}$  (in 1D)

Lecture 34: Laws of the day:

ex: Faraday's law of electrophoresis:

System:  $\mu^{(0)}$  is constant, molecules have molar charge  $z$  in potential  $V_0 = -x \cdot E$

1.  $\mu_i = \mu_i^{(0)} + z V_0$   
 $\frac{\partial z}{\partial x} V_0 = 0$ , since molar charge is constant

2.  $\frac{d\mu_i}{dx} = 0 + z \frac{dV_0}{dx} = z \cdot (-E) = -zE$

$J = -V_c \frac{d\mu_i}{dx} = \frac{cUzE}{V} = cV$

$v_{\text{drift}} = V_c E = \frac{-z}{8} E$  (Faraday's law)

ex: Ohm's Law:

Current  $\left( \frac{C}{s} \right) \propto$  Flux  $\left( \frac{\text{molar}}{\text{m}^2 \cdot \text{s}} \right)$

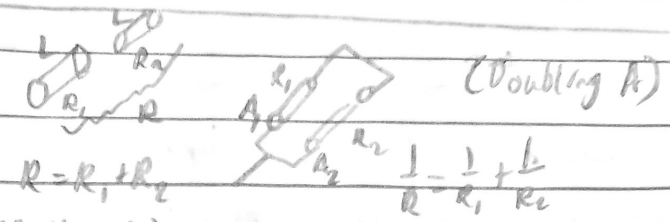
$I = z \left( \frac{C}{\text{mol}} \right) \cdot J \left( \frac{\text{molar}}{\text{m}^2 \cdot \text{s}} \right) \cdot A (\text{m}^2)$

$= z \cdot cV \cdot A$   
 $= z \cdot cUzE \cdot A$   
 $= z^2 cU \frac{V_0}{L} \cdot A$

$I = \frac{V_0}{R} \Leftrightarrow IR = V_0$  (Ohm's law)  
 $R = \frac{L}{z^2 c U A}$

$R = \frac{LRT}{z^2 c U A}$  (T with T)  
 $T \rightarrow 0, R \rightarrow 0$  (superconductor)

$\frac{Lk_B T}{z^2 c U A}$



ex: Nernst Equation (concentration form)

1.  $\mu_i = \mu_i^{(0)} + RT \ln c_i(x) + z_i V_0$

2.  $\frac{d\mu_i}{dx} = 0 + RT \frac{dc_i}{dx} + z_i \frac{dV_0}{dx}$

$J = -V_c c_i \left( RT \frac{dc_i}{dx} + z_i \frac{dV_0}{dx} \right)$

$J = 0$  at equilibrium

$\rightarrow \frac{dV_0}{dx} = \frac{-RT}{z_i} \frac{dc_i}{dx}$  (integrate from 0 to x on both sides)

$\rightarrow \int_0^x dx' \frac{dV_0}{dx'} = \frac{-RT}{z_i} \int_0^x \frac{dc_i}{dx'}$

$V_0(x) - V_0(0) = \frac{-RT}{z_i} (\ln c_i(x) - \ln c_i(0))$

$V_0(x) = V_0(0) - \frac{RT}{z_i F} \ln \frac{c_i(x)}{c_i(0)}$

↑ integer charge  
 ↑ Faraday's constant

