L 34: review

deriving equilibrium, Steady State & Transport

1) Find $\mu_i$ $(W(E) \rightarrow E(w) \rightarrow E(S) \rightarrow G(T))$

$$\mu_{g_i}(x) \leftarrow \frac{\partial G}{\partial n_i} = \mu_i$$

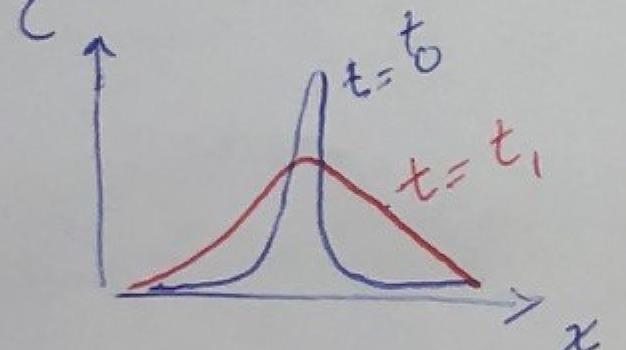
2) Get flux: $J_i = c_i v_i = -u_i c_i \frac{\partial \mu_{g_i}}{\partial x}$

Also, use $\underbrace{\frac{\partial c}{\partial t} + \frac{\partial J}{\partial x} = 0}_{\text{continuity}}$ as needed.

ex: $\mu = \mu^\circ + RT \ln c(x) \Rightarrow$

$$J = -uRT \frac{\partial c}{\partial x} = -D \frac{\partial c}{\partial x}$$

$$\xrightarrow{\text{continuity}} \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$ "Fick's law"




from this one can derive the c(x) as a function of time

Today and next lecture: "Any law you want!"

ex #1: Faraday's law (again)

$$Z = q \cdot F \rightarrow 94\,600 \ \frac{\text{coulombs}}{\text{mole}}$$

$q \rightarrow \pm 1, \pm 2, \ldots$

$Z$: molar charge $\left(\frac{\text{coulomb}}{\text{mole}}\right)$

for one material: (no "i" subscript)

$$\mu_g = \mu^\circ + Z \cdot V_e(x)$$

($V_e$: applied potential)

$$\Rightarrow \frac{\partial \mu_g}{\partial x} = Z \frac{\partial V_e}{\partial x} \Rightarrow J = -u \cdot c \frac{d\mu_g}{dx}$$

$$\xrightarrow{V_e(x) = -x \cdot \mathcal{E}} J = -u \cdot c \cdot (-\mathcal{E} \cdot Z) = u c \mathcal{E} Z$$

$$\xrightarrow{J = c \cdot v_{drift}} v_{drift} = Z \cdot u \cdot \mathcal{E}$$

ex #2 : Ohm's law

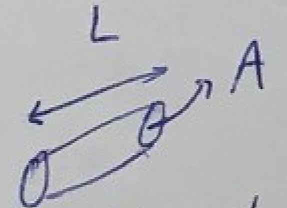
$$I = z \cdot J \cdot A = z \cdot c\, v \cdot A$$

$I \rightarrow \frac{\text{coulomb}}{\text{second}}$, $z \rightarrow \frac{\text{coulomb}}{\text{mole}}$, $J \rightarrow \frac{\text{mole}}{m^2 \cdot s}$, $A \rightarrow m^2$

$$= z\, c\, z\, u\, \mathcal{E}\, A$$

$$= z^2 c \cdot u \underbrace{\frac{V_e}{L}}_{\mathcal{E}} \cdot A$$

$\mathcal{E} = \frac{V_e}{L}$ :




$\Delta V_e = L \cdot \mathcal{E}$

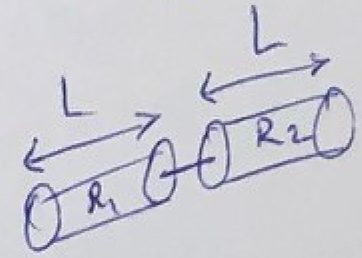
$$\Rightarrow I \cdot \underbrace{\frac{L}{z^2 \cdot c \cdot u \cdot A}}_{} = V_e \quad \text{OR} \quad I \cdot R = V_e$$

resistance $\leftarrow R \equiv \frac{L\,RT}{z^2 c D A}$

where $u$ is replaced by $\frac{D}{RT}$

gas constant $\leftarrow RT$

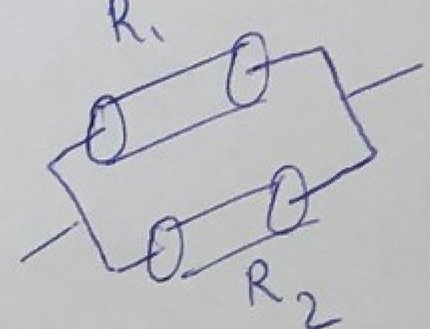
Thought experiment: resistance of resistors in series and in parallel




"in series"

$R_{total} = R_1 + R_2 = 2R$

$(\text{if } R_1 = R_2)$




$$R \sim \frac{1}{A} \Rightarrow \frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} = \frac{2}{R}$$

$(\text{if } R_1 = R_2)$

L stays same

ex #3 : Nernst equation

c depends on x and applied Voltage

exists:

1) $\mu_i = \mu_i^0 + RT \ln c_i(x) + z_i \cdot \underbrace{V_e}_{-x\mathcal{E}}$

2) $\frac{d\mu_i}{dx} = RT \frac{\partial \ln c_i}{\partial x} + z_i \frac{\partial V_e}{\partial x}$

$\xrightarrow{\text{in equilibrium}}$ $J = -u_i c_i \left(RT \frac{\partial \ln c_i}{\partial x} + z_i \frac{\partial V_e}{\partial x}\right) = 0$

equilibrium

$z_i = q_i F$

$$\Longrightarrow \frac{\partial V_e}{\partial x} = -\frac{RT}{q_i F}\frac{\partial \ln c_i}{\partial x} \Longrightarrow$$

$$\int_0^x dx' \frac{\partial V_e}{\partial x'} = -\frac{RT}{q_i F}\int_0^x dx' \frac{\partial \ln c_i}{\partial x'}$$

$$\Longrightarrow V_e(x) - V_e(0) = -\frac{RT}{q_i F} \ln \frac{C_i(x)}{C_i(0)}$$

$X = 0$ ; standard conditions( $C(0) = 1 \frac{mol}{L}$)

$$V_e = V^0 - \frac{RT}{q_i F} \ln C_i \quad \text{"Nernst eq."}$$