Chapter 4

\[ J_i = \text{gradient of } \bar{\mu}_i \quad \text{or} \quad J_i = \nabla \bar{\mu}_i \quad \nabla \text{ unit vector for cement in} \quad 3-D \]

\[ \bar{\mu}_2 = \bar{\mu}_2^0 + RT \ln \frac{\bar{\mu}_2}{\bar{\mu}_2^0} + z_i F \Phi \]

\[ J_i (x) = - \left( \frac{C_i}{D_i} \right) \frac{\partial \bar{\mu}_i}{\partial x} \quad \text{(-) direction & flux opposes direction of increasing } \bar{\mu}_i \]

\[ \frac{\partial}{\partial x} \left\{ - D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i}{R} \frac{F D_i C_i(x)}{RT} \right\} \]

\[ \frac{\partial}{\partial x} \left\{ \frac{C_i(x)}{D_i} \right\} \quad \frac{\partial}{\partial x} \left\{ \frac{C_i(x)}{D_i} \right\} \quad \text{convection} \]

\[ \text{Migration} \]

\[ \frac{-j_i}{z_i FA} = \frac{i_{d,i}}{z_i FA} + \frac{i_{m,i}}{z_i FA} \]

\[ \frac{i_{d,i}}{z_i FA} = D_i \left( \frac{\partial C_i}{\partial x} \right) \bigg|_{x=0} \]

\[ \frac{i_{m,i}}{z_i FA} = \frac{z_i F D_i C_i(x)}{RT} \bigg|_{x=0} \]

\[ u_i = \frac{|z_i| F D_i}{RT} \quad \text{mobility} \quad \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \]

\[ \frac{(C/\text{mol}) \text{cm}^2 \text{V}^{-1} \text{s}^{-1}}{(J/m^2 \text{V}^{-1}) (x)} = \frac{(\text{cm}^2 \text{s}^{-1})}{V} = \frac{\text{cm}^2}{V \cdot \text{s}} \]

\[ j_i = |z_i| FA u_i C_i \left( \frac{\partial \Phi}{\partial x} \right) \]
High supporting electrolyte concentration nearly eliminates \( \frac{2d}{dx} \), also makes \( R_m \) small so that \( E_{real} = E_{eq} - iR_m \).

\[
\frac{dx}{dx} = \frac{\Delta E}{E}
\]

\[
i_j = \frac{1}{Z_j} F A u_j C_j \frac{\Delta E}{E} \quad \text{one ionic species}
\]

\[
i_{form} = \sum_{j=1}^{1} i_j = \frac{F A \Delta E}{E} \sum_j \left| Z_j \right| u_j C_j \quad \text{some of concentrations}
\]

\[
\text{conductance} = \frac{L}{R(\Omega)} = L = \frac{i_{form}}{\Delta E} = \frac{FA}{E} \sum_j \left| Z_j \right| u_j C_j = \frac{A}{2} \kappa
\]

\[
\kappa = \text{conductivity} = F \sum_j \left| Z_j \right| u_j C_j \quad \text{[S}^{-1} \text{cm}^{-1}] \]

\[
P = \text{resistivity} = \frac{L}{K} \quad \frac{1}{\kappa}
\]

\[
R = \text{resistance} = \frac{P}{\kappa} \quad \frac{1}{i_{form}} = \frac{1}{\sum_j \left| Z_j \right| u_j C_j}
\]

\[
t_j = \text{transference number}
\]

\[
i = i_d + i_m
\]

\[
i = i_d - i_m
\]

\[
i = i_d
\]

\[
\text{Cu}_{2}^{+} + 2e^{-} \rightarrow \text{Cu}
\]

\[
\text{Cu(CN)_{4}}^{2-} + 2e^{-} \rightarrow \text{Cu} + 4\text{CN}^{-}
\]

\[
\text{Cu(CN)_{2}} + 2e^{-} \rightarrow \text{Cu} + 2\text{CN}^{-}
\]
Both migration and diffusion can be present in an ecosystem.

\[
\frac{N(x,t)}{N_0} = \exp \left( \frac{-x^2}{4Dt} \right)
\]

\[e^{-x} \rightarrow 0 \text{ as } x \rightarrow \infty\]

\[M_d = U_d = \frac{\Delta}{t} = \left( \frac{2D_d}{t} \right)^{1/2} \quad \text{diffusional velocity (collisions)}\]

\[M_m = U_m = \frac{|z| FD_i \xi RT}{\text{migration velocity}}\]

\[U_m \ll U_d\]

\[\left( \frac{|z| FD_i \xi}{RT} \right) \ll \left( \frac{2D_i}{t} \right)^{1/2}\]

Usually desire \( U_m \ll U_d \)

If \( \xi \) is made small compared to diffusional length

Fick's laws \( \rightarrow \) describe flux of species and its concentration as a function of time and position.

\[J_o(x,t) = D_o \left( \frac{\partial c_o(x,t)}{\partial x} \right) \quad \text{1st law}\]

\[J_o(x,t) = \frac{1}{A} \left( \frac{N_o(x) - N_o(x+\Delta x)}{\Delta t} \right) \quad \text{Point of interest}\]

\[\frac{N_o(x)}{N_0(x+\Delta x)} \]
\[ \frac{\partial C_0(x,t)}{\partial t} = D_0 \left( \frac{\partial^2 C_0(x,t)}{\partial x^2} \right) \]  

2nd Law: rate of change of 1st derivative 

how fast slope is changing 

derivative 

how the concentration changes as a function of time. 

\[ OX + e^- \rightarrow \text{Red} \]

a) initial conditions 
\[ C_0(x,0) = f(x) \]
\[ C_0(x,0) = C_0^* \quad C_R(x,0) = \emptyset \quad \text{(for all } x) \]

b) semi-infinite boundary 
\[ \lim_{x \to -\infty} C_0(x,t) = C_0^* \quad \text{(at all } t) \]
\[ \lim_{x \to \infty} C_R(x,t) = \emptyset \]

c) boundary condition (surface) 
\[ C_0(0,t) = f(t) \quad C_R(0,t) = f(t) \]
\[ OX + e^- \rightarrow \text{Red} \]

\[ -J_0(0,t) = \frac{i}{nFA} = D_0 \left[ \frac{\partial C_0(x,t)}{\partial x} \right]_{x=0} = f(t) \]
\[
\left( \frac{2D}{t} \right)^{1/2} = \left( \frac{cm^2/s}{s} \right)^{1/2} = \frac{cm/s^{1/2}}{s^{1/2}} = \frac{cm}{s^{1/2}} \cdot s^{-1/2}
\]

\[
\frac{cm}{s} = \left( \frac{2D}{t} \right)^{1/2} = \frac{cm^2}{s} = \left( \frac{cm^2}{s^2} \right)^{1/2} = \frac{cm}{s^{1/2}}
\]