Irrev Øving 3

1a) $J_1 = L_{11}\frac{\partial}{\partial x}\left(\frac{\mu_1}{T}\right) + L_{12}\frac{\partial}{\partial x}\left(\frac{\mu_2}{T}\right)$

$J_2 = L_{21}\frac{\partial}{\partial x}\left(\frac{\mu_1}{T}\right) + L_{22}\frac{\partial}{\partial x}\left(\frac{\mu_2}{T}\right)$

1b) $\sigma = \sum J_i x_i \geq 0$

$\sigma = \sum_i x_i \sum_k L_{ik} X_k \geq 0$

$X_{k \neq i} = 0 \rightarrow \sigma = X_i^2 L_{ii} \geq 0 \rightarrow L_{ii} \geq 0 \quad \square$

1c) Onsager : $L_{ij} = L_{ji}$
Conductivity-matrix is symmetric

1e) $J_1 = L_{11}X_1 + L_{12}\left(\frac{J_2 - L_{21}X_1}{L_{22}}\right)$

1d) $L_{12} = L_{21} = 0 \rightarrow$ No coupling between J_1 and J_2

1f) $L_{11}L_{22} - L_{12}^2 = \det(L) = 0$
$\rightarrow$ L is not invertible
$\rightarrow$ Fluxes are not independent or one of the fluxes is zero and the process is reversible.

2a) $\vec{J} = L\vec{X}$, $\vec{J} = \begin{pmatrix} J_1 \\ \vdots \\ J_n \end{pmatrix}$, $\vec{X} = \begin{pmatrix} x_1 \\ \vdots \\ x_n \end{pmatrix}$

$\vec{X} = L^{-1}\vec{J}$, $L = \begin{bmatrix} L_{11} & \cdots & L_{1n} \\ \vdots & \ddots & \vdots \\ L_{n1} & \cdots & L_{nn} \end{bmatrix}$

2b) $\nearrow$

2c) $\underline{R = L^{-1}}$

Oppg. 3a)

0,1M KCl 0,1M HCl	0,1M KCl

"klassisk": $\mu = \frac{1}{2}\sum c_i z_i^2 \rightarrow \mu_L = 0{,}2M,\ \mu_R = 0{,}1M$

$\gamma_\pm = \exp\left(z_+ z_- \sqrt{\frac{\mu}{\mu_{DH}}}\right),\ \mu_{DH} = 0{,}727M$

$\gamma_\pm^L = 0{,}59\ ,\ \gamma_\pm^R = 0{,}69$

$a_{K^+}^L = 0{,}059\ ,\ a_{K^+}^R = 0{,}069$

$a_{H^+}^L = 0{,}059\ ,\ a_{H^+}^R = 0$

Net diffusion: $\xleftarrow{K^+}$ $\xrightarrow[H^+]{}$

Irrev: $J_{K^+} = -\frac{L_{KK}}{T}\frac{\partial \mu_{T,K}}{\partial x} - \frac{L_{KH}}{T}\frac{\partial \mu_{T,H}}{\partial x} - \frac{L_{KC}}{T}\frac{\partial \mu_{T,Cl}}{\partial x}$

$J_{H^+} = -\frac{L_{HK}}{T}\frac{\partial \mu_{T,K}}{\partial x} - \frac{L_{HH}}{T}\frac{\partial \mu_{T,K}}{\partial x} - \frac{L_{HC}}{T}\frac{\partial \mu_{T,Cl}}{\partial x}$

$J_{Cl^-} = 0 = -\frac{L_{CK}}{T}\frac{\partial \mu_{T,K}}{\partial x} - \frac{L_{CH}}{T}\frac{\partial \mu_{T,K}}{\partial x} - \frac{L_{CC}}{T}\frac{\partial \mu_{T,Cl}}{\partial x}$

$\frac{\partial}{\partial x}\mu_{T,i} = \frac{\partial}{\partial x}(\mu_i^\circ + RT\ln a_i) = RT\frac{1}{a_i}\frac{\partial a_i}{\partial x}$

$$\begin{pmatrix} J_{K^+} \\ J_{H^+} \\ 0 \end{pmatrix} = -R\underline{L}\begin{pmatrix} \frac{1}{a_{K^+}}\frac{\partial a_{K^+}}{\partial x} \\ \frac{1}{a_{H^+}}\frac{\partial a_{H^+}}{\partial x} \\ \frac{1}{a_{Cl^-}}\frac{\partial a_{Cl^-}}{\partial x} \end{pmatrix}$$

Oppg. 3c)

$$\Delta\tilde{\mu}_{HCl} = \Delta\tilde{\mu}_{HCl} = 0$$

$$\tilde{\mu}_i = \tilde{\mu}_i^0 + RT\ln\prod_j a_j + Fz_i\phi,\quad i = \{K^+, H^+\}$$

$$a_i \approx \gamma_\pm C_i\ ,\quad \gamma_\pm = \exp\left(z_+ z_- \sqrt{\frac{\mu}{\mu_{OH}}}\right)$$

$$\mu = \frac{1}{2}\sum C_i z_i^2$$

Ionic strength of solution

Debye-Hückel mean activity coefficient

$$\left.\begin{aligned} C_i^L &= C_i^{L,0} - \Delta C_i \\ C_i^R &= C_i^{R,0} + \Delta C_i \end{aligned}\right\} \Delta C_i > 0 \rightarrow \text{transport from left to right}$$

$$\frac{d\phi}{dx} = \frac{\rho}{\varepsilon}\ ,\quad \rho = F\sum C_i z_i\ ,\quad \rho = \text{charge density}$$

$$\hookrightarrow \Delta\phi = \frac{F}{\varepsilon}\left(\sum (C_i^L - C_i^R) z_i\right)$$

I) $$\Delta\mu_{K^+} = 0 = RT\ln\left(\frac{\gamma_\pm^L C_{K^+}^L}{\gamma_\pm^R C_{K^+}^R}\right) + \frac{F^2}{\varepsilon}\sum (C_i^L - C_i^R) z_i$$

II) $$\Delta\mu_{H^+} = 0 = RT\ln\left(\frac{\gamma_\pm^L C_{H^+}^L}{\gamma_\pm^R C_{H^+}^R}\right) + \frac{F^2}{\varepsilon}\sum (C_i^L - C_i^R) z_i$$

Solve I and II for ΔC_{H^+} and ΔC_{K^+} with python:

$$C_{K^+}^L = 0{,}13\,M\ ,\quad C_{K^+}^R = 0{,}07\,M$$

$$C_{H^+}^L = 0{,}07\,M\ ,\quad C_{H^+}^R = 0{,}03\,M$$

3b)

$$J_{H^+} = \frac{-L_{HH}}{T}\frac{\partial\mu_{H^+,T}}{\partial x} - \frac{L_{HK}}{T}\frac{\partial\mu_{K^+,T}}{\partial T}$$

$$J_{K^+} = -\frac{L_{KH}}{T}\frac{\partial\mu_{H^+,T}}{\partial x} - \frac{L_{KK}}{T}\frac{\partial\mu_{K^+,T}}{\partial T}$$

Oppg. 4a) $\sum n_i d\mu_i = Vdp - SdT$

$\sum c_i d\mu_i = dp - sdT$

4b) two, because $\sum x_i = 1$ reduces the ammount of independent concentrations by one.

4c) two, because $j = F \sum z_i J_i$ is dependent on the mass-fluxes and $\frac{d\phi}{dx}$ is dependent on the concentration gradients. (or one if Solvent F.O.R. is chosen)

4d) three/two using Lab/Solvent F.O.R.

5a) $\begin{pmatrix} J_1 \\ J_2 \end{pmatrix} = \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \begin{pmatrix} X_1 \\ X_2 \end{pmatrix} \rightarrow \begin{pmatrix} X_1 \\ X_2 \end{pmatrix} = \frac{1}{L_{11}L_{22} - L_{12}^2} \begin{bmatrix} L_{22} & -L_{21} \\ -L_{12} & L_{11} \end{bmatrix} \begin{pmatrix} J_1 \\ J_2 \end{pmatrix}$

$$X_2 = \frac{L_{11}J_2 - L_{12}J_1}{L_{11}L_{22} - L_{12}^2}, \quad J_1 = L_{11}X_1 + L_{12}X_2$$

$$X_2 = \frac{L_{11}J_2 - L_{12}L_{11}X_1 - L_{12}^2 X_2}{L_{11}L_{22} - L_{12}^2} = \frac{L_{11}J_2 - L_{11}L_{12}X_1}{L_{11}L_{22} - L_{12}^2}$$

$$J_1 = L_{11}X_1 + L_{12}\left(\frac{L_{11}J_2 - L_{11}L_{12}X_1}{L_{11}L_{22} - L_{12}^2}\right)$$

$$\sigma = \sum J_i X_i = L_{11}X_1^2 + \left(\frac{L_{11}L_{12}}{L_{11}L_{22} - L_{12}^2}\right)J_2 X_1 - \left(\frac{L_{11}L_{12}}{L_{11}L_{22} - L_{12}^2}\right)X_1^2$$
$$+ \left(\frac{L_{11}}{L_{11}L_{22} - L_{12}^2}\right)J_2^2 - \left(\frac{L_{11}L_{12}}{L_{11}L_{22} - L_{12}^2}\right)J_2 X_2 .$$

$$\sigma = \left(L_{11} - \frac{L_{11}L_{12}}{L_{11}L_{22} - L_{12}^2}\right)X_1^2 + \left(\frac{L_{11}}{L_{11}L_{22} - L_{12}^2}\right)J_2^2$$

Oppg. 5b) $X_1 = -\frac{1}{T}\frac{\partial \mu_1}{\partial x}$, $J_2 = j$

$$\left(\frac{L_{11}}{L_{11}L_{22}-L_{12}^2}\right) > 0$$

Can be interpreted as lost work resulting from j, a kind of electrical resistance

$$\left(L_{11} - \underbrace{\frac{L_{11}L_{12}}{L_{11}L_{22}-L_{12}^2}}\right) > 0$$

$\rightarrow$ Reversible charge transfer (lowers σ)

$\uparrow$

Irreversible mass transfer

third term cancelled in 5a