

Irrev Spring 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

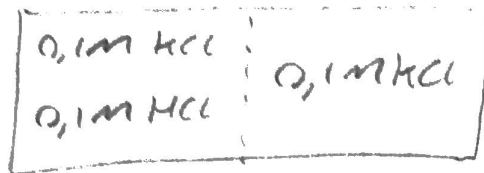
$\rightarrow$ Fluxes are not independent
or one of the Fluxes is zero and
the process is reversible.

2a) $\vec{J} = L \vec{X}$, $\vec{J} = \begin{pmatrix} J_1 \\ \vdots \\ J_n \end{pmatrix}$, $\vec{X} = \begin{pmatrix} x_1 \\ \vdots \\ x_n \end{pmatrix}$
 $\vec{X} = L^{-1} \vec{J}$, $L = \begin{bmatrix} L_{11} & \dots & L_{1n} \\ \vdots & \ddots & \vdots \\ L_{n1} & \dots & L_{nn} \end{bmatrix}$

2b) $\nearrow$

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

Oppg. 3a)



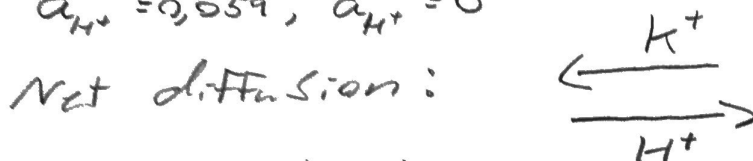
"klassisk": $\mu = \frac{1}{2} \sum c_i z_i^2 \rightarrow \mu_L = 0,2 M, \mu_R = 0,1 M$

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

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

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

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



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

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

$$J_C = 0 = -\frac{L_{CK}}{T} \frac{\partial \mu_{T,K}}{\partial x} - \frac{L_{CH}}{T} \frac{\partial \mu_{T,H}}{\partial x} - \frac{L_{CC}}{T} \frac{\partial \mu_{T,C}}{\partial x}$$

$$\frac{\partial}{\partial x} \mu_{T,i} = \frac{\partial}{\partial x} (\mu_i^0 + RT \ln a_i) = RT \frac{1}{a_i} \frac{\partial a_i}{\partial x}$$

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

Oppg. 3c)

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

$$\tilde{\mu}_i = \tilde{\mu}_i^0 + RT \ln T a_i + F z_i \phi, i = \{K^+, H^+\}$$

$$a_i \approx \gamma_{\pm} C_i, \quad \gamma_{\pm} = \exp\left(z_+ z_- \sqrt{\frac{\mu}{\mu_{0H}}}\right)$$

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

↑ Ionic strength
of solution

↑ Debye-Hückel mean
activity coefficient

$$\left. \begin{aligned} C_i^L &= C_i^{L0} - \Delta C_i \\ C_i^R &= C_i^{R0} + \Delta C_i \end{aligned} \right\} \Delta C_i > 0 \rightarrow \text{transport from left to right}$$

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

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

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

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

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

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

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

$$3b) \quad J_{H^+} = \frac{-L_{HH}}{T} \frac{\partial \mu_{H^+,T}}{\partial x} - \frac{L_{HK}}{T} \frac{\partial \mu_{H^+,T}}{\partial T}$$

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

Oppg. 4a) $\sum n_i d\mu_i = V dp - S dT$
 $\sum c_i d\mu_i = dp - s dT$

4b) two, because

$\sum x_i = 1$ reduces the amount 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) $\begin{pmatrix} j_1 \\ j_2 \end{pmatrix} = \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \rightarrow \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \frac{1}{L_{11}L_{22} - L_{12}^2} \begin{bmatrix} L_{22} & -L_{21} \\ -L_{12} & L_{11} \end{bmatrix} \begin{pmatrix} j_1 \\ j_2 \end{pmatrix}$

$x_2 = \frac{L_{11}j_2 - L_{12}j_1}{L_{11}L_{22} - L_{12}^2}, \quad j_1 = L_{11}x_1 + L_{12}x_2$

$x_2 = \frac{L_{11}j_2 - L_{12}L_{11}x_1 - L_{12}^2x_2}{L_{11}L_{22} - L_{12}^2} = \frac{L_{11}j_2 - L_{11}L_{12}x_1}{L_{11}L_{22} - L_{12}^2}$

$j_1 = L_{11}x_1 + L_{12} \left(\frac{L_{11}j_2 - L_{11}L_{12}x_1}{L_{11}L_{22} - L_{12}^2} \right)$

$\sigma = \sum j_i x_i = L_{11}x_1^2 + \left(\frac{L_{11}L_{12}}{L_{11}L_{22} - L_{12}^2} \right) j_2 x_1 - \left(\frac{L_{11}L_{12}}{L_{11}L_{22} - L_{12}^2} \right) x_1^2$
 $+ \left(\frac{L_{11}}{L_{11}L_{22} - L_{12}^2} \right) j_2^2 - \left(\frac{L_{11}L_{12}}{L_{11}L_{22} - L_{12}^2} \right) j_2 x_2$

$\sigma = \left(L_{11} - \frac{L_{11}L_{12}}{L_{11}L_{22} - L_{12}^2} \right) x_1^2 + \left(\frac{L_{11}}{L_{11}L_{22} - L_{12}^2} \right) j_2^2$

Oppg. 58) $X_1 = -\frac{1}{T} \frac{\partial \mu_1}{\partial x}$, $J_2 = j$

$\left(\frac{L_{11}}{L_{11}L_{22} - L_{12}^2} \right) > 0$ Can be interpreted as lost work resulting from j , a kind of electrical resistance

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

↑
Irreversible mass transfer

↘ Reversible charge transfer (lowers α)

third term cancelled in 5a