CHEM-E4235 Transport processes at electrodes and membranes

Exercises from Chapter 1 and 2

1. Prove that $\sum_{i=1}^{k} M_i \vec{j}_i^m = 0$, where M_i is the molar mass of species i and $\vec{j}_i^m = c_i(\vec{v}_i - \vec{v})$ is its flux in mass-average (barycentric) reference frame. $\vec{v} = \sum_{i=1}^{k} w_i \vec{v}_i$; w_i is the mass fraction, $w_i = \frac{m_i}{\sum_k m_k}$.

   Hint: Express w_i in terms of concentrations and molar masses.

2. Prove that electric current density $\vec{I}$ does not depend on the reference frame: $\vec{I} = F\sum_{i=1}^{k} z_i \vec{j}_i^r$ with any reference velocity $\vec{v}^r$.

3. Prove eq. (1.68): $-\sum_i \vec{j}_i^m \cdot \nabla\mu_i + \vec{I}\cdot\vec{E} = -\sum_i \vec{j}_i^m \cdot \nabla\tilde{\mu}_i$.

4. In the case of two fluxes and forces the phenomenological equations are written as

   $$\begin{cases} J_1 = L_{11}X_1 + L_{12}X_2 \\ J_2 = L_{21}X_1 + L_{22}X_2 \end{cases}$$

   What constraints are required from the phenomenological coefficients L_{ij} in order to make the dissipation function $\theta > 0$. Remember Onsager's reciprocal relation $L_{ij} = L_{ji}$. Hint: Since the eigenvalues of matrix **L**, λ_1 and $\lambda_2 > 0$, also $\lambda_1\lambda_2 > 0$ and $\lambda_1 + \lambda_2 > 0$.

5. The molar conductivities (Λ) of NaCl, $CaCl_2$, Na_2SO_4 and $CaSO_4$ have been measured at infinite dilution. Prove that it is not possible to determine the ionic molar conductivities (λ_i) from these measurements. $\Lambda = \sum_i \upsilon_i \lambda_i$. Hint: Create a matrix equation.

6. In a ternary system of two 1:1 electrolytes, e.g. NaCl-KCl, the fluxes of the components are written in the phenomenological form as

$$\begin{cases} -\vec{J}_{13} = L_{13,13}\nabla\mu_{13} + L_{13,23}\nabla\mu_{23} & (2.103) \\ -\vec{J}_{23} = L_{13,23}\nabla\mu_{13} + L_{23,23}\nabla\mu_{23} & (2.104) \end{cases}$$

and in Fickian formalism as

$$\begin{cases} -\vec{J}_{13} = D_{13,13}\nabla c_{13} + D_{13,23}\nabla c_{23} \\ -\vec{J}_{23} = D_{23,13}\nabla c_{13} + D_{23,23}\nabla c_{23} \end{cases}$$

[NaCl] = c_{13} and [KCl] = c_{23}, i.e. $z_1 = \upsilon_1 = z_2 = \upsilon_2 = -z_3 = \upsilon_{3,1} = \upsilon_{3,2} = 1$, and therefore $c_1 = c_{13}$, $c_2 = c_{23}$, $c_3 = c_{13} + c_{23}$. The phenomenal coefficients are given by eqs. (2.108) – (2.110) in the textbook. As an example, prove eq. (2.113) when we know that

$$D_{13,13} = RT\left[L_{13,13}\left(\frac{\upsilon_1}{c_{13}} + \frac{\upsilon_{3,1}^2}{c_3}\right) + L_{13,23}\frac{\upsilon_{3,1}\upsilon_{3,2}}{c_3}\right]$$

Hint: You need to apply the definitions of the transport number and conductivity, eqs. (2.72) and (2.73). Note that Onsager's theorem applies to L_{ij}s but not to D_{ij}s.