Non-equilibrium thermodynamics
Exercise 3
Transport Equations

1

The flux equations for transport of two solutes can be written \( J_i = \sum_{j=1}^{2} L_{ij} X_j, (i = 1, 2) \).

a) Write out the equations in detail.
b) Why must \( L_{11} \) and \( L_{22} \) always be positive?
c) What is the Onsager reciprocal relations?
d) What does it mean if \( L_{12} = 0 \)?
e) Express \( J_1 \) as a function of \( X_1 \) and \( J_2 \).
f) Under what conditions do we have \( L_{11} L_{22} - L_{12}^2 = 0 \)?

2

a) Express the forces as linear functions of all fluxes. Use a system with 3 independent fluxes and forces as example.
b) Show how the equations can be written on matrix form.
c) What is the relation between the resistivity matrix and the conductivity matrix?

3

Two aqueous solutions of equal volume are separated by a purely cation-selective membrane. Initially the lefthand-side solution contains 0.1 kmol m\(^{-3}\) KCl and 0.1 kmol m\(^{-3}\) HCl, while the righthand-side solution contains only 0.1 kmol m\(^{-3}\) KCl. The temperature can be assumed constant throughout the system.
a) Give the directions of net diffusion for K$^+$ and H$^+$ in the membrane.

b) After some time, but before equilibrium has been attained, give the driving force for the diffusion of H$^+$ from left to right. What is the driving force for the diffusion of K$^+$ from right to left?

c) Give the condition for equilibrium in terms of differences in chemical potentials. Calculate the concentrations of KCl and HCl on both sides of the membrane at equilibrium, assuming ideal solutions. For ideal solutions, $\Delta \mu_{HCl} = -RT \ln(c_{H^+,l}c_{Cl^-,l}/c_{H^+,r}c_{Cl^-,r})$, and similar for $\Delta \mu_{KCl}$. $l$ is lefthand-side solution and $r$ is righthand-side solution. Neglect any transfer of H$_2$O.

4

a) Write the Gibbs - Duhem equation.

b) A tube contains a mixture of the neutral species A, B and C. The composition is different in the two ends of the tube. At constant temperature and pressure a diffusion takes place, levelling out the difference in composition. How many independent forces for diffusion are there?

c) The tube contains the species Na$^+$, Cl$^-$ and H$_2$O. How many independent forces for diffusion are there in this case?

d) The tube contains Na$^+$, K$^+$, Cl$^-$ and H$_2$O. How many independent forces for diffusion are there now?

5

Consider a system with two independent fluxes and forces.

a) Express the entropy production by $X_1$, $J_2$ and coefficients. Collect the result in three terms, the first term does not contain $J_2$, the second term does not contain $X_1$, while the third term contains $X_1J_2$.

b) Assume that $X_1 = -\frac{1}{T} \frac{\partial \mu}{\partial x}$ and that $J_2 = j$. Give a physical interpretation of terms one and two, and give the sign (plus or minus) for each term. Use the Onsager reciprocal relations and find the value of the third term.