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 aquous 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_2O.

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_2O. How many independent forces for diffusion are there in this case?

d) The tube contains Na^+, K^+, Cl^- and H_2O. 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 $X_1 = -\frac{1}{T}\frac{\partial\mu_1}{\partial x}$ 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.