

Solution to exercise 1

1.?

2.

a) The first law efficiency is

$$\eta_I = \frac{w}{q} = \frac{25\text{MW}}{73\text{MW}} = 0.34$$

b) Provided that we can regard the heat as delivered from a high temperature reservoir, the ideal work is:

$$w_{ideal} = \left(\frac{T - T_0}{T}\right)q = \left(1 - \frac{8 + 273}{1150 + 273}\right) = 58.6 \text{ MW}$$

and the second law efficiency is

$$\eta_{II} = \frac{w}{w_{ideal}} = \frac{25}{58.6} = 0.43$$

The lost work is accordingly:

$$w_{lost} = w_{ideal} - w = 58.6 - 25 = 23.6 \text{ MW} = T_0 \frac{dS_{irr}}{dt}$$

giving the entropy production

$$\frac{dS_{irr}}{dt} = \frac{23.6 \text{ MW}}{281 \text{ K}} = 0.084 \text{ MW/K}$$

The reversible limit of the first law efficiency is the Carnot efficiency, while the Reversible limit of the second law efficiency is unity.

Solution to Exercise 2

1. The conjugate force to both fluxes is $\frac{d}{dx} \frac{1}{T}$

This shows that one must speak of sets of conjugate fluxes and forces that define the entropy production- There are several equivalent sets.

The conjugate force to the electric current is always, $-\frac{d}{dx} \frac{\varphi}{T}$ while the conjugate flux to $-\frac{d}{dx} \frac{\mu_j}{T}$ is the diffusion flux.

2. The thermodynamic driving forces are always obtained from the entropy production. The forces in the simple transport law, are set from Experiment. The difference will appear in the expression and the dimension, but they formulations can be made compatible through the Choice of the transport coefficient (cf. Lecture 3)

3. Consider one dimensional stationary state transport. The total entropy production is calculated by introducing Fourier's law for the flux:

$$\Omega \int_0^d \sigma dx = \Omega J'_q \int_0^d \frac{d}{dx} \left(\frac{1}{T} \right) dx = \Omega J'_q \int_{T_h}^{T_c} d \left(\frac{1}{T} \right)$$

$$\Omega J'_q \int_{T_h}^{T_c} d \left(\frac{1}{T} \right) = -\Omega \lambda \frac{\Delta T}{d} \left[\frac{1}{T_c} - \frac{1}{T_h} \right]$$

$$= -0.03 \cdot 273 \frac{(-50)}{0.01} \left[\frac{1}{373} - \frac{1}{423} \right] = 11 \text{ W/K}$$

$$w_{lost} = 293 \cdot 11 = 3.2 \text{ kW}$$

Heating by electricity is “costly”, since the energy can be used to do work.

Solution to exercise 3

Given two fluxes and two forces:

$$J_1 = L_{11}X_1 + L_{12}X_2$$

$$J_2 = L_{21}X_1 + L_{22}X_2$$

We eliminate the second force:

$$X_2 = -(L_{21} / L_{22})X_1 + J_2 / L_{22}$$

$$J_1 = -(L_{11} - L_{21}L_{12} / L_{22})X_1 + J_2L_{12} / L_{22}$$

And use this to express the entropy production:

$$\sigma = J_1X_1 + J_2X_2$$

$$= (L_{11} - L_{12}L_{21} / L_{22})X_1^2 + J_2^2 / L_{22}$$

Onsager relations were also used

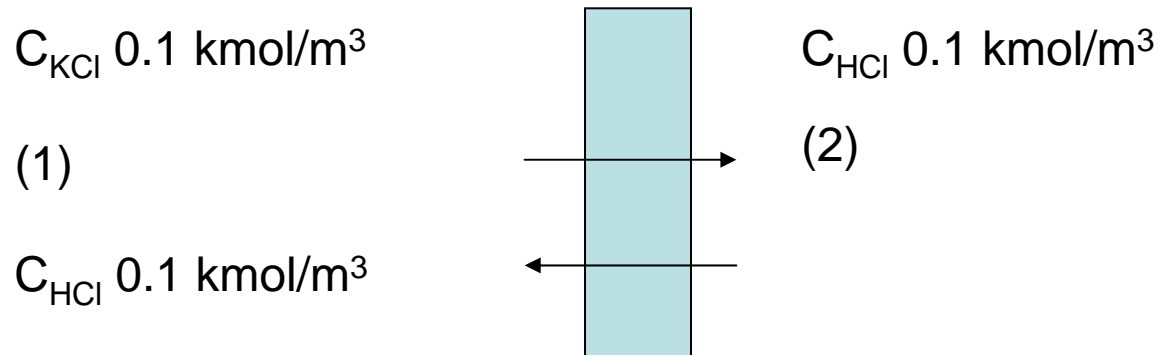
The expression is always positive, for any values of the forces or the fluxes, including zero. This gives

$$(L_{11} - L_{12}L_{21} / L_{22}) \geq 0, \quad L_{22} \geq 0$$

We have chosen the number 1 or 2 randomly. Therefore are all main coefficients positive. A zero coupling coefficient means that no work can be done.

$$(L_{11} - L_{12}L_{21} / L_{22}) = 0 \rightarrow J_1 = \frac{L_{12}}{L_{22}} J_2$$

This is called complete coupling



The properties of the membrane are such that only cation transport is allowed. Which means that the net flux of KCl must be exactly equal and opposite of the flux of HCl (the cations define the component concentration).

$$J_{KCl} = L_{11} \left(-\frac{1}{T} \frac{d\mu_{KCl}}{dx} \right) + L_{12} \left(-\frac{1}{T} \frac{d\mu_{HCl}}{dx} \right)$$

$$J_{HCl} = L_{21} \left(-\frac{1}{T} \frac{d\mu_{KCl}}{dx} \right) + L_{22} \left(-\frac{1}{T} \frac{d\mu_{HCl}}{dx} \right)$$

$$J_{KCl} + J_{HCl} = 0 = (L_{11} + L_{21}) \left(-\frac{1}{T} \frac{d\mu_{KCl}}{dx} \right) + (L_{12} + L_{22}) \left(-\frac{1}{T} \frac{d\mu_{HCl}}{dx} \right)$$

The last identity is true for any value of the forces, since we can change the concentration of the salts as we want. Therefore:

$$L_{11} + L_{21} = 0, \quad L_{12} + L_{22} = 0$$

$$J_{KCl} = -L_{11} \frac{1}{T} \left(\frac{d\mu_{KCl}}{dx} - \frac{d\mu_{HCl}}{dx} \right)$$

$$J_{HCl} = -L_{12} \frac{1}{T} \left(\frac{d\mu_{KCl}}{dx} - \frac{d\mu_{HCl}}{dx} \right)$$

$$c_{KCl,tot} = 0.1 = c_{K^+}(1) + c_{K^+}(2)$$

$$c_{HCl,tot} = 0.2 = c_{H^+}(1) + c_{H^+}(2)$$

$$0.2 = c_{K^+}(1) + c_{H^+}(1)$$

$$0.1 = c_{H^+}(2) + c_{K^+}(2)$$

$$c_{K^+}(1) = c_{H^+}(2)$$

Mass balances in the absence of volume changes

The electroneutrality conditions give one extra relation

$$\Delta\mu_{KCl} = \Delta\mu_{HCl}$$

$$RT \ln \frac{c_{K^+}(2)c_{Cl^-}(2)}{c_{K^+}(1)c_{Cl^-}(1)} = RT \ln \frac{c_{H^+}(2)c_{Cl^-}(2)}{c_{H^+}(1)c_{Cl^-}(1)}$$

$$\frac{c_{K^+}(2)}{c_{K^+}(1)} = \frac{c_{H^+}(2)}{c_{H^+}(1)}$$

$$c_{K^+}(1) = 0.067 \text{ kmol/m}^3, \quad c_{K^+}(2) = 0.033 \text{ kmol/m}^3$$

$$c_{H^+}(1) = 0.133 \text{ kmol/m}^3, \quad c_{H^+}(2) = 0.067 \text{ kmol/m}^3$$

The balance of forces gives the fourth equation needed to solve the unknown concentrations.