Non-Equilibrium Thermodynamics: Foundations and Applications.

Lecture 8: Transport of mass and charge

Signe Kjelstrup

Department of Chemistry,
Norwegian University of Science and Technology,
Trondheim, Norway

and

Engineering Thermodynamics
Department of Process and Energy, TU Delft

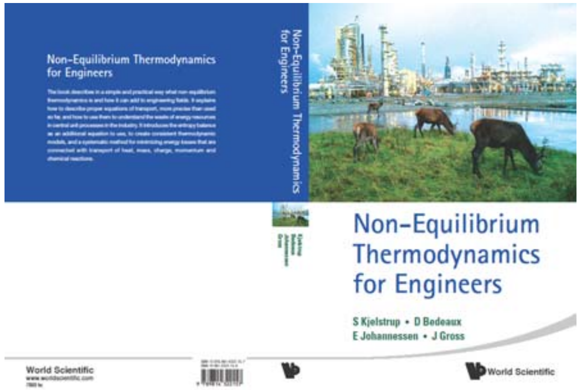
http://www.chem.ntnu.no/nonequilibrium-thermodynamics/

Non-Equilibrium Thermodynamics: Foundations and Applications

	Tuesday, Sept. 7	Wednesday, Sept. 8	Thursday, Sept.9	Friday, Sept.10
9:00-10:30	Why non-equilibrium ther-modynamics?	Transport of heat and mass	Transport of heat and charge	Entropy produc-tion minimization theory
11:00-12:30	Entropy production for a homogeneous phase	Multi-component heat and mass diffusion	Transport of mass and charge	Entropy produc-tion minimization. Examples.
16:00-17:00	Flux equations and Onsager relations	Power from regular and thermal osmo-sis	Modeling the polymer electrolyte fuel cell	

Lecture 8. Transport of mass and charge

Chapter 4.6

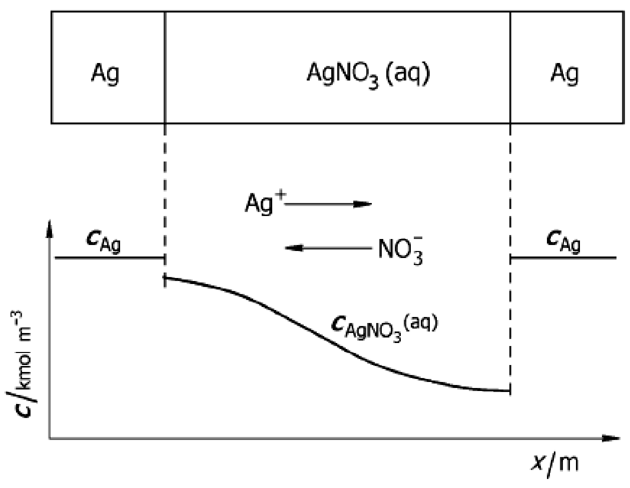


Chapter 10

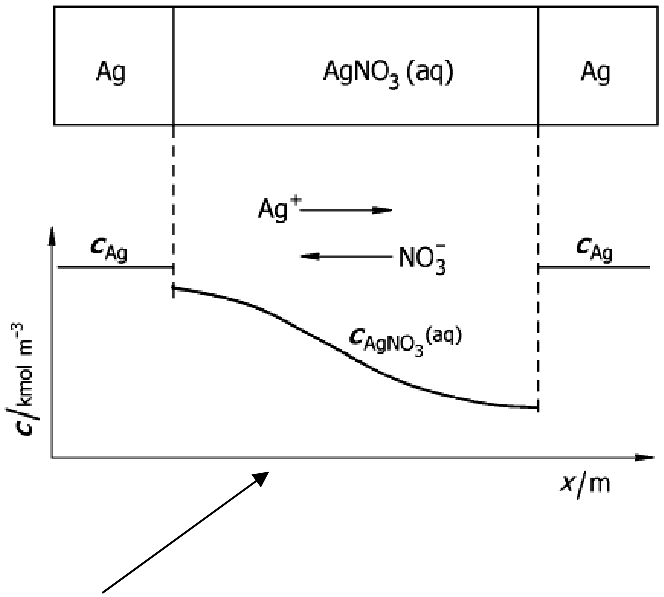
Exercise

Your working procedure

1. The entropy production
2. The fluxes
3. The coefficients
4. Can the system perform work (separation)?
5. What happens if we add work to the system?



Potential work is lost by diffusion and conduction



Two electrodes of silver in a non-uniform solution of silver nitrate

- The energy available for work in this concentration cell lies in the concentration gradient of the salt.
- Diffusion will after some time make the system homogeneous.
- Electric conduction affects the potential

The entropy production of the isothermal cell

The electric potential difference between two electrodes separated by d*x*

$$\sigma = J_1\left(-\frac{1}{T}\frac{d}{dx}\mu_1\right) + j\left(-\frac{1}{T}\frac{d\phi}{dx}\right)$$

Component one is transported.
The flux of the second component
is the frame of reference.

The electric current density does not depend on the frame of reference

The coupled flux equations

A common factor 1/*T* is absorbed in the transport coefficients

$$J_1 = -L_{\mu\mu}\frac{\partial \mu_1}{\partial x} - L_{\mu\phi}\frac{\partial \phi}{\partial x}$$

$$j = -L_{\phi\mu}\frac{\partial \mu_1}{\partial x} - L_{\phi\phi}\frac{\partial \phi}{\partial x}$$

Relation to Fick's and Ohm's law:

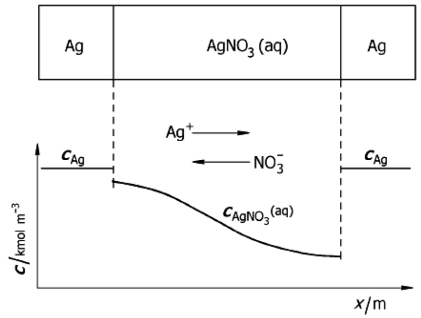
$$J_1 = -D\frac{\partial c_1}{\partial x} = -L_{\mu\mu}\frac{\partial \mu_1}{\partial x} = -\left(L_{\mu\mu}\frac{\partial \mu_1}{\partial c_1}\right)\frac{\partial c_1}{\partial x}$$

$$j = -L_{\phi\phi}\frac{\partial \phi}{\partial x}$$

Onsager relations

$$L_{\mu\phi} = L_{\phi\mu}$$

The mass flux



- Diffusion and charge transfer are superimposed:

$$J_1 = -L_{\mu\mu}\frac{\partial \mu_1}{\partial x} - L_{\mu\phi}\frac{\partial \phi}{\partial x}$$

$$j = -L_{\phi\mu}\frac{\partial \mu_1}{\partial x} - L_{\phi\phi}\frac{\partial \phi}{\partial x}$$

$$J_1 = -\left(L_{\mu\mu} - \frac{L_{\mu\phi}L_{\phi\mu}}{L_{\phi\phi}}\right)\frac{\partial \mu_1}{\partial x} + \frac{L_{\mu\phi}}{L_{\phi\phi}}\, j$$

Coupling reduces the diffusion coefficient

Coupling gives an electric current

The two ions diffuse together!

Each ion take part in the charge transport!

The electric work

$$J_1 = -L_{\mu\mu}\frac{\partial \mu_1}{\partial x} - L_{\mu\phi}\frac{\partial \phi}{\partial x}$$

$$j = -L_{\phi\mu}\frac{\partial \mu_1}{\partial x} - L_{\phi\phi}\frac{\partial \phi}{\partial x}$$

Defining the transference coefficient of the salt

$$t_1 = \left[\frac{J_1}{j}\right]_{d\mu_1 = 0} = \frac{L_{\mu\phi}}{L_{\phi\phi}}$$

The electric work in V (for one faraday transferred):

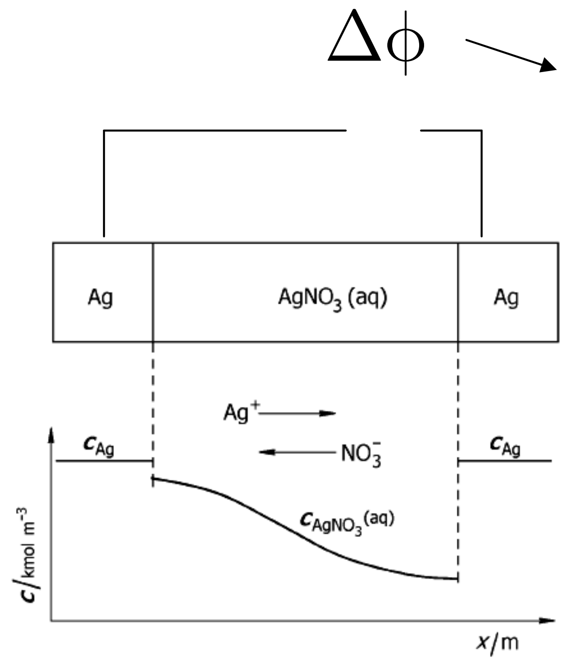
$$\Delta\phi = \int_L \frac{\partial \phi}{\partial x} dx = -\int_L \left[t_1 \frac{\partial \mu_1}{\partial x} - \frac{1}{L_{\phi\phi}} j \right] dx$$

Useful work from the gradient of chemical potential

We used the Onsager relation

Ohmic potential drop

The electric work of a concentration cell



A concentration cell has a potential difference of some mV

The transference coefficient is minus the transport number of the nitrate ion

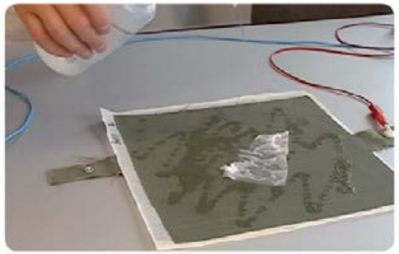
Useful work from the gradient of chemical potential

$$\Delta\phi = \int_L \frac{\partial \phi}{\partial x} dx = -\int_L \left[t_1 \frac{\partial \mu_1}{\partial x} - \frac{1}{L_{\phi\phi}} j \right] dx$$

Water can be moved by passing an electric current, cf. lecture 1.
Can transport of water create electric work?

We define the water transference coefficient of a component from the flux when electric charge (i.e. protons) carry charge across an ion-exchange membrane:

$$t_1 = \left[\frac{J_1}{j} \right]_{d\mu_1 = 0} = \frac{L_{\mu\phi}}{L_{\phi\phi}}$$



EO-textile test-cell: A 30x30 cm piece of EO-textile with a paper tissue on top is sprayed with water.

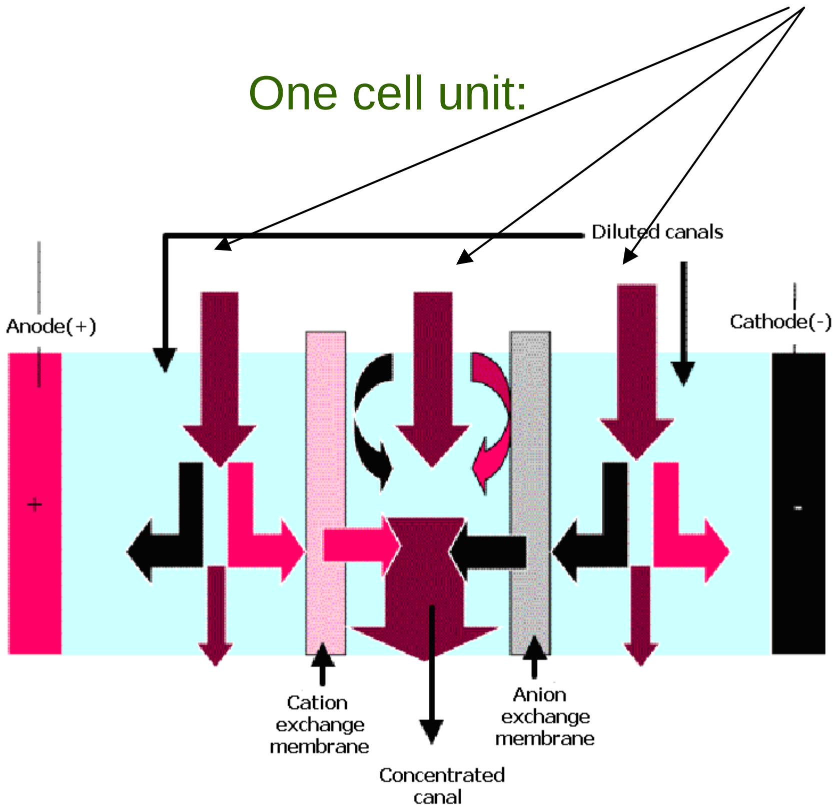
The expression for the work is the same as before:

$$\Delta\phi = \int_L \frac{\partial \phi}{\partial x} dx = -\int_L \left[t_1 \frac{\partial \mu_1}{\partial x} - \frac{1}{L_{\phi\phi}} j \right] dx$$

This picture is shot after 17 seconds of EO pumping.

After 28 seconds the textile surface is dry, and most of the water has been removed from the paper on top.

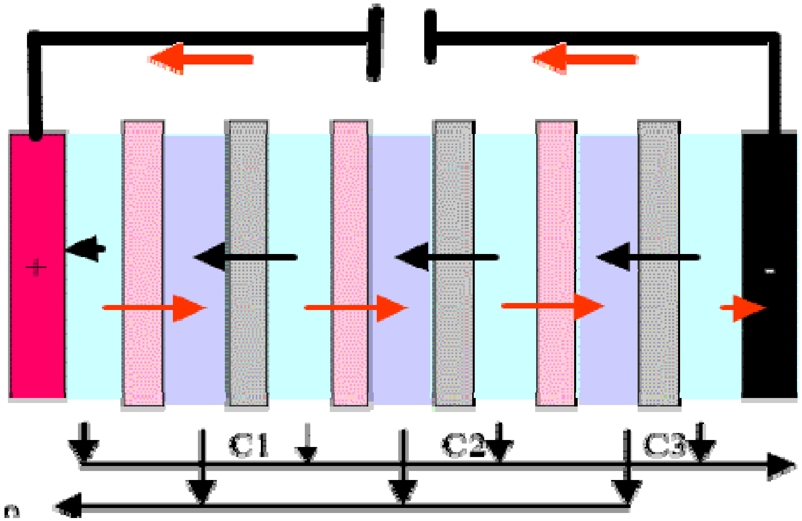
Producing pure water from salt water: Electrodialysis



- Sea water is fed to a system of ion exchange membranes permeable for cations or anions
- By applying electric current, salt is moved against its gradient in chemical potential to create pure(r) water

Reverse electrodialysis (RED): Exploiting the salt gradient to do work

Multiple cell units



- The electric potential of the plant is proportional to the number of unit cells
- The voltage over a unit is appr. 160 mV. It is possible to have 500 units in series

Summary

- The transport of mass and charge were described by the fluxes and forces from the entropy production
- The origin of electric work in systems with transport of mass and charge is the coupling coefficent, here the transference coefficient of the component
- This coupling coefficient can be of the same order of magnitude as the main coefficients
- We have studied concentration cells only. High transferenece coefficients (transport numbers) are important for all batteries and fuel cells (formation cells).

Exercise for Lecture 8

1. Calculate the work obtainable by moving water in an ion exchange membrane against a pressure difference of 3 bar. The water transference coefficient is 2.6, Faraday's constant is 96500 C/mol, the molar volume of water is 18 10^{-6} m^3/mol.
2. Calculate the electric work obtainable from a single unit of an electrodialysis cell at 300 K. Consider the ion exchange membranes to be perfect. Electrodes are reversible to chloride. The salt concentration in sea is 0.55 mol/m^3. At that concentration and temperature 300 K, the mean activitity coefficient is 0.681. The salt concentration in the compartment where river water is coming in is 0.001 mol/m^3.