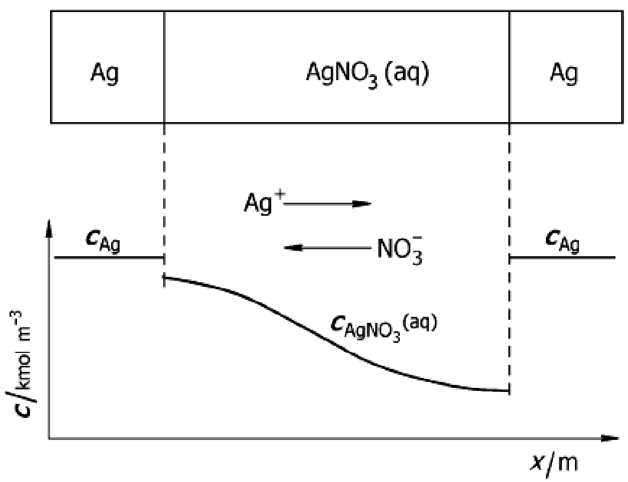
Non-Equilibrium Thermodynamics for Engineers

Lecture 5

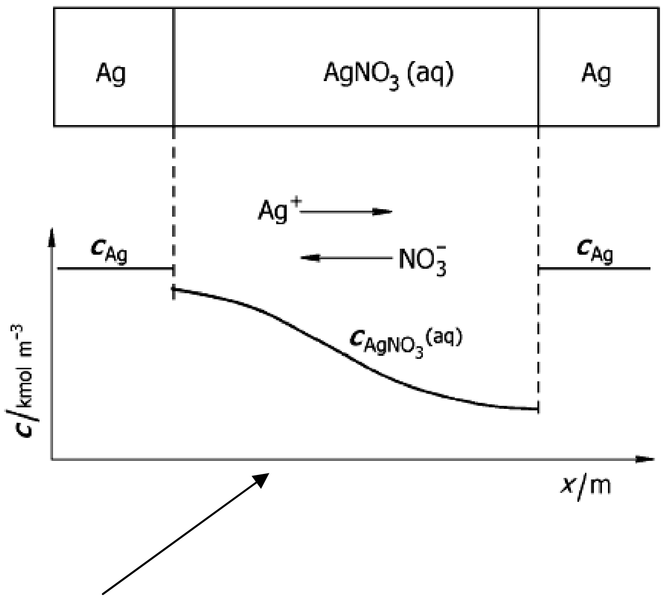
Signe Kjelstrup
Chair of Engineering Thermodynamics
Department of Process and Energy
TU Delft

Transport of mass and charge

1. The entropy production
2. The fluxes
3. The coefficients
4. Electric work from chemical energy in an electrochemical cell:



Potential work can be lost by diffusion in this cell



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.

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:

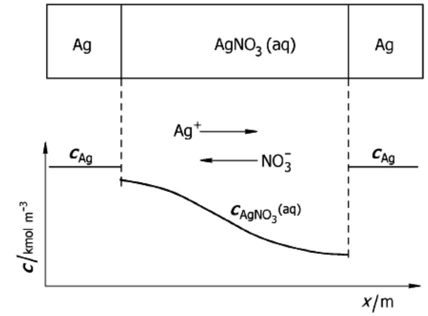
$$J_1 = -D\frac{\partial c_1}{\partial x} = -L_{\mu\mu}\frac{\partial \mu_1}{\partial x} = -\left(L_{\mu\mu}\frac{RT}{c_1}\frac{\partial \mu_1}{\partial c_1}\right)\frac{\partial c_1}{\partial x}$$

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

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

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

Useful work from the gradient of chemical potential

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

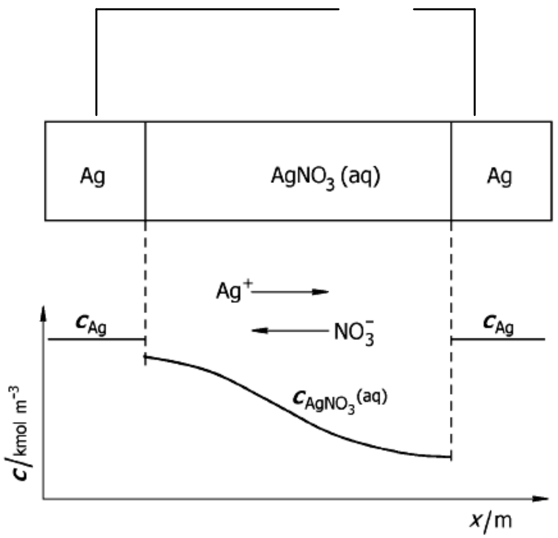
$$\Delta\phi = \int_L \frac{\partial \phi}{\partial x}dx = -\int_L \left[t_1 \frac{\partial \mu_1}{\partial x} - \frac{1}{L_{\phi\phi}} j\right]dx$$

We used the Onsager relation

Ohmic potential drop

The electric work

$\Delta\phi$



A concentration cell has a potential difference of some mV

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

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

Useful work from the gradient of chemical potential

Can transport of water create electric work?

We can define the water transference coefficient when electric charge (i.e. protons) carry charge across an ion-exchange membrane:

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

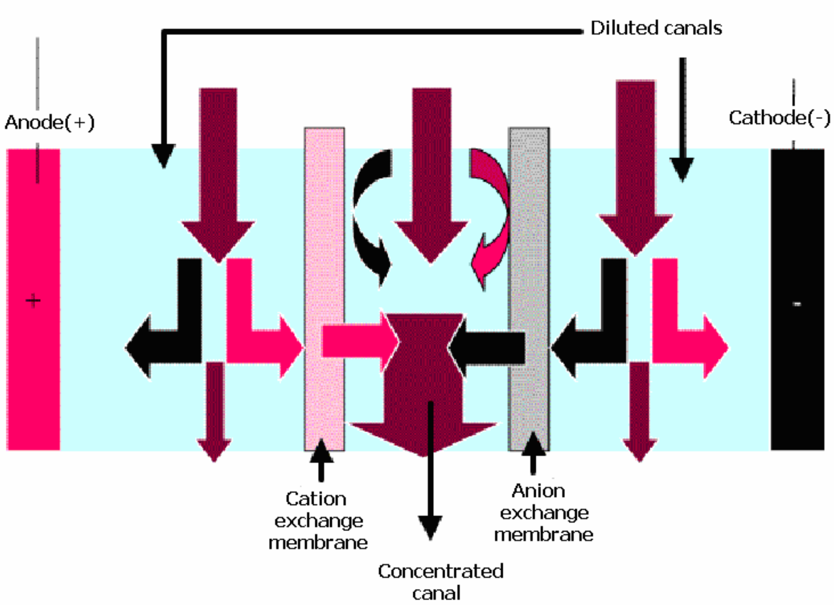
The expression for the work is the same:

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

The transference coefficient can be larger than unity, but the gradient In chemical potential of water is normally small. Show that!

Reverse electrodialysis

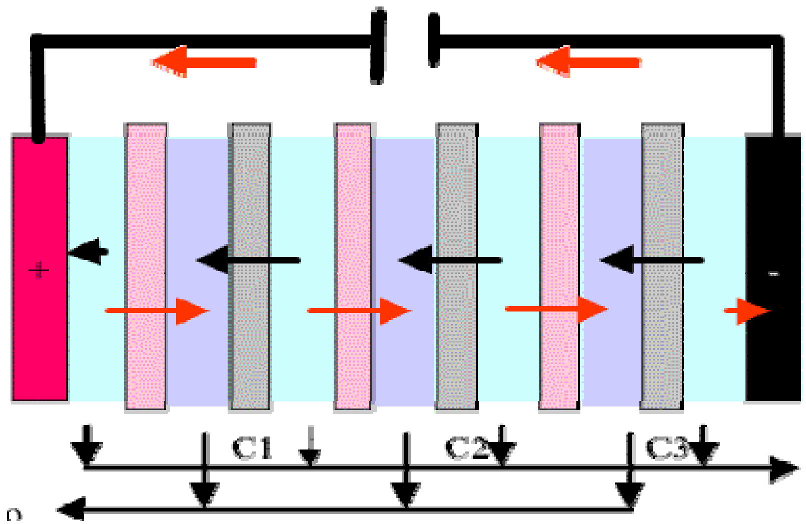
One cell unit:



- Alternating chambers with sea water and river water, separated by ion exchange membranes permeable for cations or anions
- Gradient in chemical potential drives the ions through the membranes and generate a voltage corresponding to the potential chemical energy

Reverse electrodialysis

Multiple cell units



- The electric potential of the plant is proportional to the number of cell units
- The voltage over one membrane is appr. 80 mV, and it's possible to have 1000 membranes in a serie

Summary

- The transport phenomena are described by the fluxes and forces in the entropy production
- The origin of electric work in systems with transport of mass and charge is the coupling coefficent, or the transference coefficient.
- The coupling coefficient is of the same order of magnitude as the other transport coefficients
- We have studied concentration cells only. A high transport number is important for all batteries and fuel cells.