

Non-Equilibrium Thermodynamics: Foundations and Applications.

Lecture 6: Power from regular and thermal osmosis

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 thermodynamics?	Transport of heat and mass	Transport of heat and charge	Entropy production minimization theory
11:00-12:30	Entropy production for a homogeneous phase	Multi-component heat and mass diffusion	Transport of mass and charge	Entropy production minimization. Examples.
16:00-17:00	Flux equations and Onsager relations	Power from regular and thermal osmosis	Modeling the polymer electrolyte fuel cell	

Non-Equilibrium Thermodynamics: Foundations and Applications

6. Power from regular and thermal osmosis

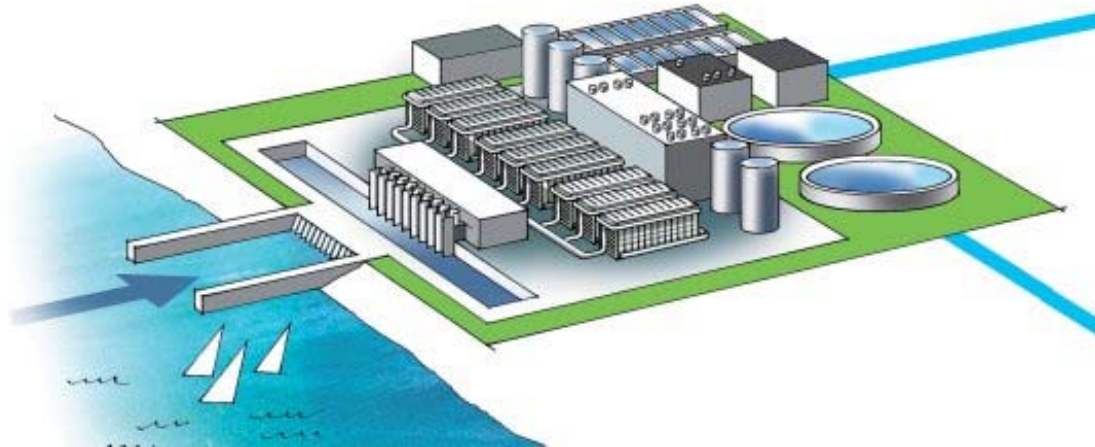
Chapter 18



Exercise

A new renewable power source from mixing river water and salt water

$$\begin{aligned}W_{ideal} &= -\Delta G_{mix} \approx T \Delta S_{mix} = RT \ln x_w \\ &= 30.8 \text{ J/mol}\end{aligned}$$

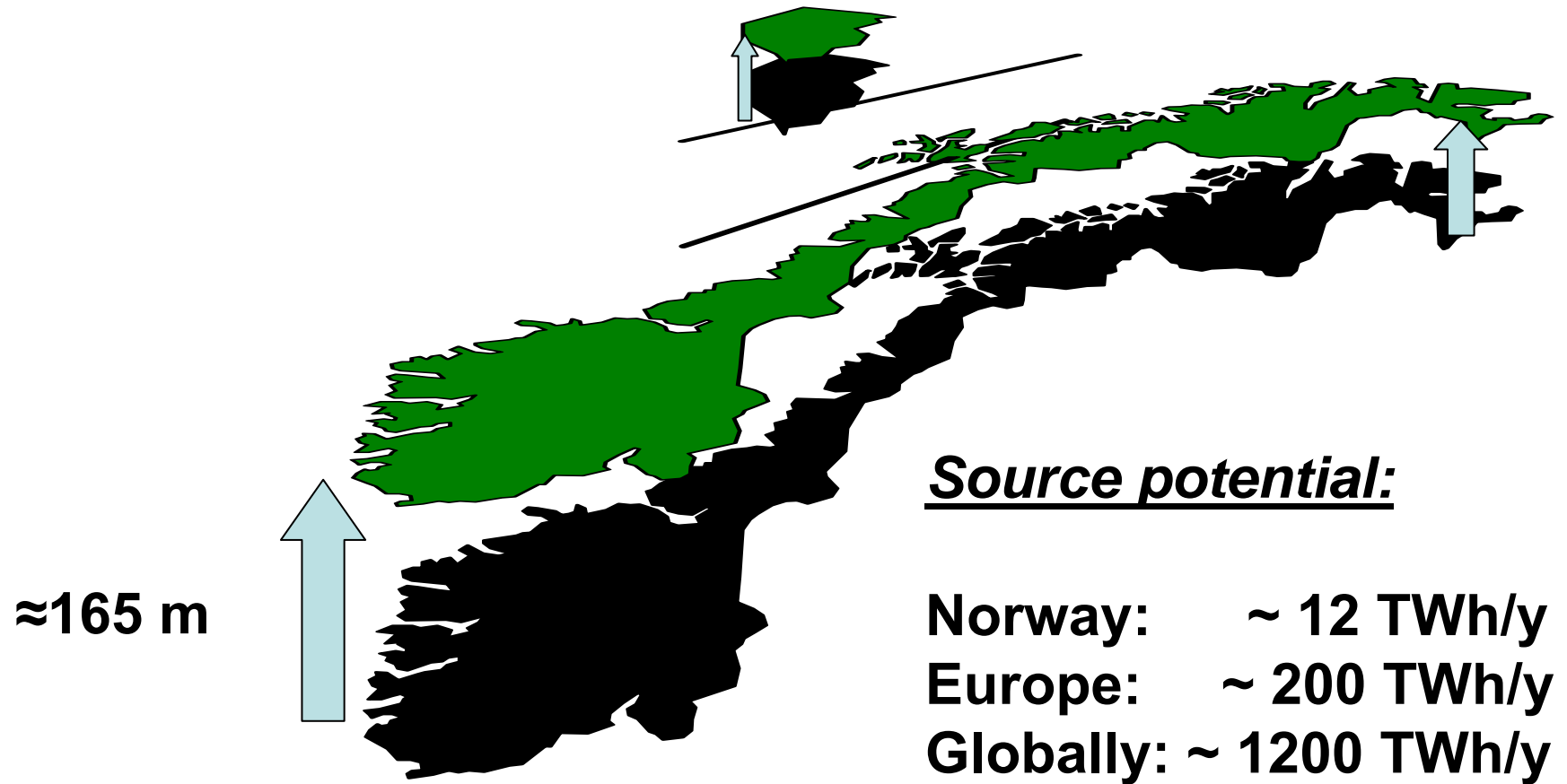


Fresh water: 55.5 kmol/m^3

Salt water: 54.9 kmol/m^3

1 m^3 can be lifted $\sim 165 \text{ m}$ (20°C)

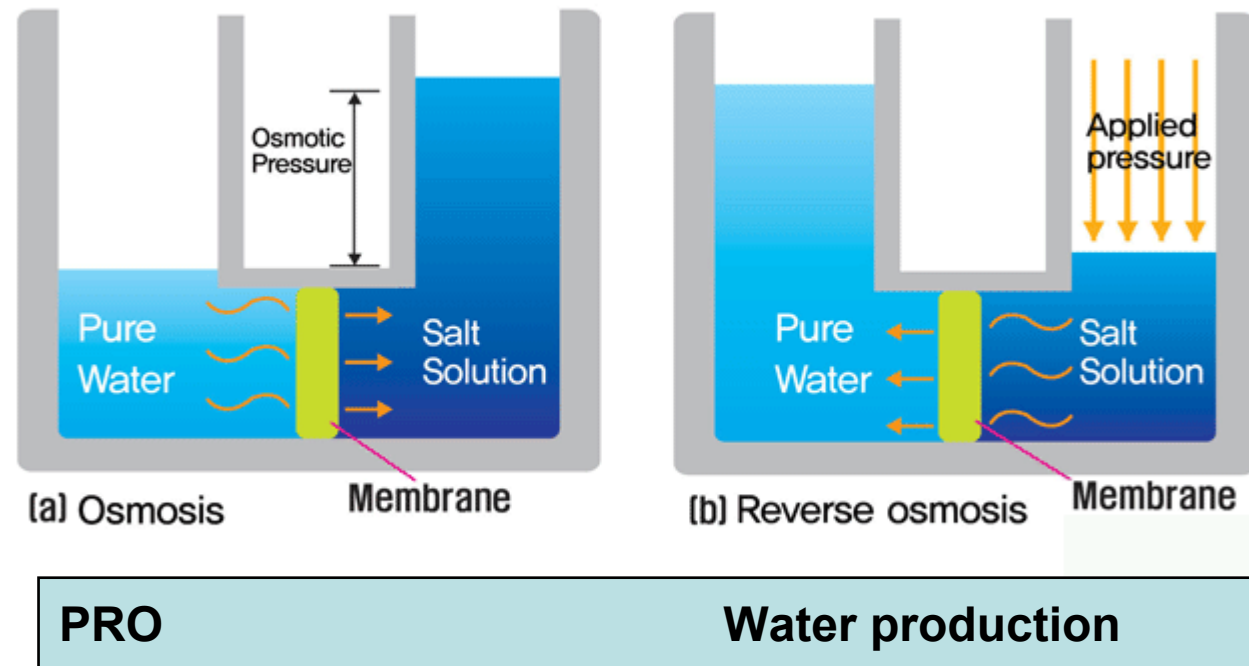
Potential



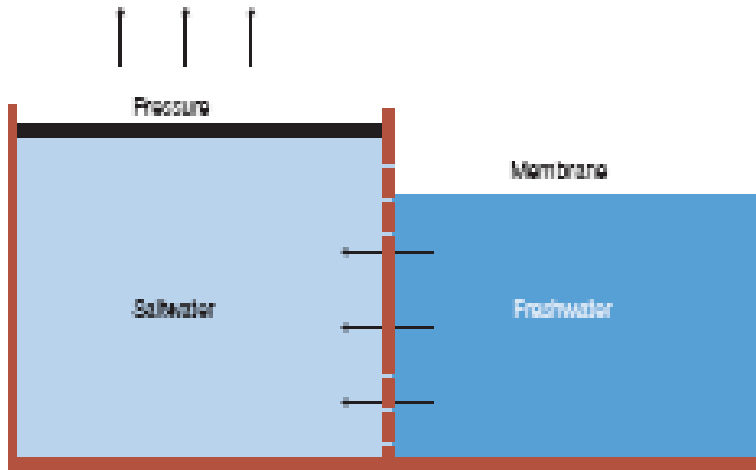
Two plant types

- Osmotic power plants
(Pressure retarded osmosis, PRO)
 - *Uses water flow (osmosis).*
 - *Technology development goes back 30 years*
 - *Statkraft, Norway, has been active since 1997*
- Reverse electrodialysis plants (cf. Lecture 8)
 - *Uses salt movement*
 - *Old idea, recent technology*
 - *Dutch technology leadership by Wetsus*

Osmosis and reverse osmosis



- Semipermeable membrane retains salt
- A net flow of water arise to the salt water side; one driving force, one flux
- Pressure increases spontaneously on the salt water side, depending on the salt concentration, and retards the flow (PRO)



Pressure retarded osmosis

The entropy production and the osmotic flux

$$\sigma = J_w \frac{d}{dx} \left(-\frac{\mu_{w,T}}{T} \right)$$

$$J_w = l \frac{d}{dx} \left(-\frac{\mu_{w,T}}{T} \right)$$

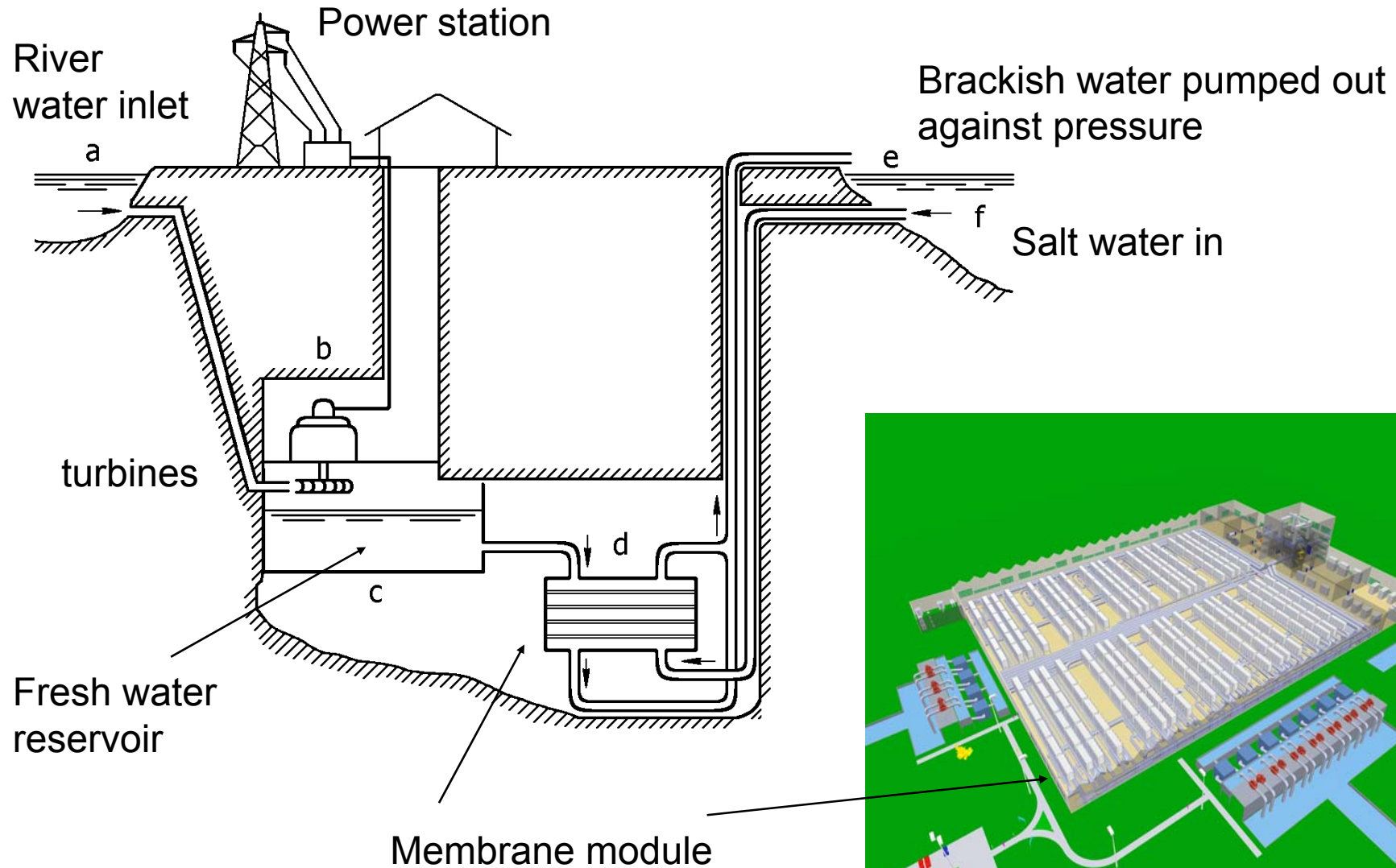
Equilibrium condition:

$$\mu_w(1: sea) = \mu_w(2: river)$$

$$\mu_w^0 + RT \ln x_w + V_w p_1 = \mu_w^0 + V_w p_2$$

$$\Pi_{J_w=0} = p_1 - p_2 = \frac{RT}{V_w} \ln x_w = \frac{8.31 \cdot 293}{18 \cdot 10^{-6}} \ln\left(\frac{54.9}{55.5}\right) \text{ Jm}^3 = 14.7 \text{ bar}$$

In practice: A pressure retarded process (PRO). Membrane plant in a sub-sea rock cavern



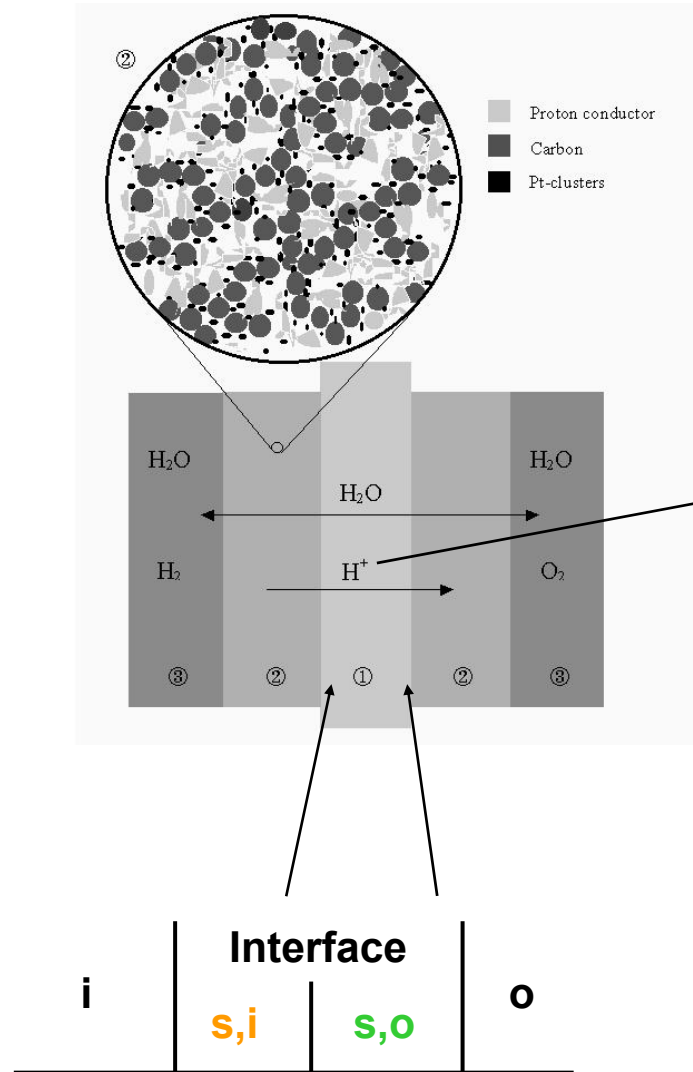
Pilot plant at Tofte, Hurum, Norway



Why develop salt power plants?

- A large power potential compared to other new renewable power sources
- Stable and predictable power production
- Competitive at 50 €/MWh in year 2020 reflecting Sustainable Energy Systems, EU FP5 Work Program
- Less dependent on external infrastructure than H₂- fuel cells and CO₂-free gas power plants
- Green certificate potential
- BUT: Needs large and costly membranes

Thermal osmosis – a second possibility?



Question: Can a difference in temperature be used to enhance power production?

Nafion, a cation exchange membrane

Transport of heat and mass across the membrane of the polymer electrolyte fuel cell

Stationary state transport *across* the interfaces:

$$\Delta_{i,o} \frac{1}{T} = r_{qq}^s J_q^i + r_{qm}^{s,l} J_m$$

$$-\frac{1}{T^o} \Delta_{i,o} \mu_{m,T} (T^o) = r_{mq}^{s,l} J_q^i + r_{mm}^{s,l} J_m$$

$$J_m^i = J_m^o = J_m, \quad J_q^i + J_m H^i = J_q^o + J_m H^o$$

Surface heat of transfer

$$q_m^{*s,i} = \left(\frac{J_q^i}{J_m} \right)_{\Delta_{i,o} T=0}$$

The surface heat of transfer, a fraction of the enthalpy of adsorption

$$q_m^{*s,o} - q_m^{*s,i} = -\Delta_{i,o} H_m$$

6+2 equations of transport for water and heat across the membrane:

$$J_q^{m,a} - J_q^{a} = J \Delta H$$

$$J_q^{c} - J_q^{m,c} = -J \Delta H$$

2 Energy balances

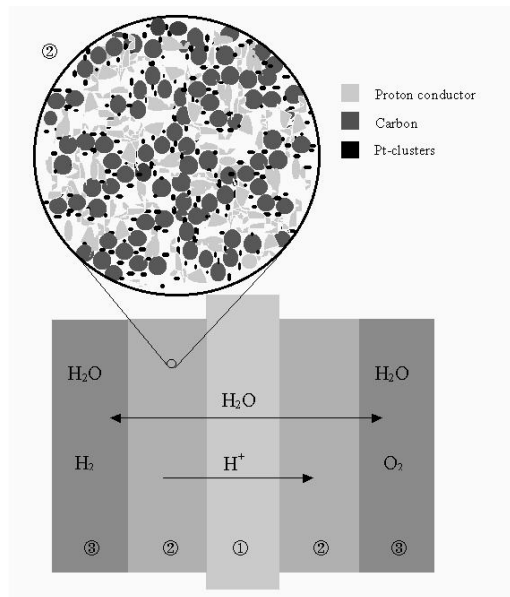
$T(x)$ -profile

$$T^{m,a} - T^a = -\frac{1}{\lambda^s} (J_q^{a} - q^{*s} J)$$

$$\frac{dT}{dx} = -\frac{1}{\lambda^m} (J_q^{m} - q^{*m} J)$$

Chemical potential profile

$$T^c - T^{m,c} = -\frac{1}{\lambda^s} (J_q^{c} - q^{*s} J)$$



Water concentration in the membrane mol/kg

$$\Delta_{a,m} \mu_T = -\frac{RT^{m,a}}{D^s c^{s,a}} J - \frac{q^{*s}}{T^{m,a}} \Delta_{a,m} T$$

$$\frac{\rho RT}{cM} \frac{d\lambda}{dx} = -\frac{RT}{cD^m} J - \frac{q^{*m}}{T} \frac{dT}{dx}$$

$$\Delta_{m,c} \mu_T = -\frac{RT^{m,c}}{D^s c^{s,c}} J - \frac{q^{*s}}{T^{m,c}} \Delta_{m,c} T$$

$$c = \rho \lambda / M$$

Polymer density, no of water molecules per polymer site, polymer weight

Experimental input

Springer et al, 1991

- **Relation between water activity a and water content λ :**

$$\lambda = 0.0043 + 17.81a - 39.85a^2 + 36.0a^3 \quad \text{for } 0 < a < 1$$

$$\lambda = 14 + 1.4(a - 1) \quad \text{for } 1 < a < 3$$

Reucroft et al, 2002

- **Enthalpy of absorption as a function of water content**

$$\Delta_{ads}H = (115 - 5\lambda)10^3 \quad \lambda < 14$$

$$\Delta_{ads}H = 45 \times 10^3 \quad \lambda > 14$$

- **Membrane thicknesses: 180 μm (Nafion 117) and 50 μm (Nafion 112)**

- **Interface thickness: 10 μm**

Springer et al, 1991

- **Membrane diffusion coefficient**

$$D^m = \exp\left(2416\left(\frac{1}{303} - \frac{1}{T}\right)\right)(2.563 - 0.33l + 0.0264l^2 - 0.000671l^3) \times 10^{-6} \quad (\text{cm}^2/\text{s}) \quad \text{for } l > 4$$

- **Membrane thermal conductivity 0.2W/K.**
- **Membrane heat of transfer -100 J/mol**
- **Interface diffusion coefficient and thermal conductivity: ten times smaller**
- **Interface heat of transfer:**
- **Water transference coefficient (electro-osmotic drag): 2.5**

$$q^{*s,i} = 0.3\Delta H$$

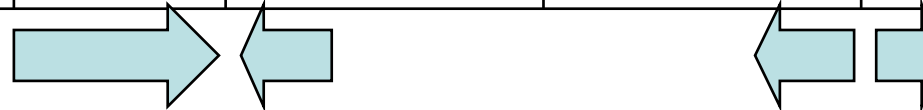
What happens when $\Delta T = 0$?

The temperature is $T = 350$ K on both sides.

Gas activities are $a^a = 0.8$ and $a^c = 1.0$

The water flux produced by this: -9.1×10^{-6} mol/m² s.

	Side a	Membrane side a	Membrane side c	Side c
Activity	0.80	0.87	0.96	1.00
Water content	7.1	9.1	12.1	14.0
Heat flux	0.44	-0.27	-0.27	0.13



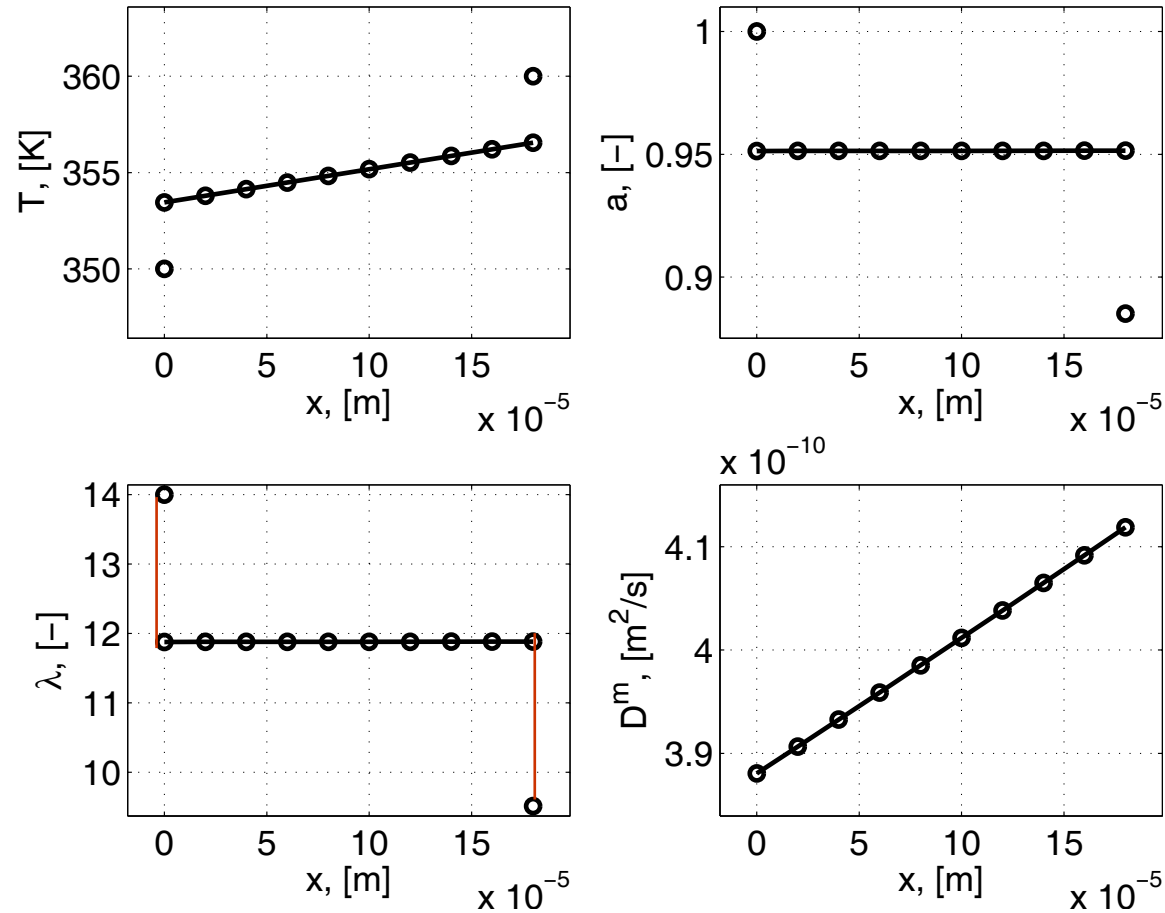
Isothermal heat transfer: Heat transfer at constant T !

The fraction of the enthalpy transported left and right is given by the coupling coefficient

What happens when $\Delta T \neq 0$? (Soret equilibrium*, cf. Lecture 4)

$$T^c - T^a = 10\text{K}$$

Temperature, activity



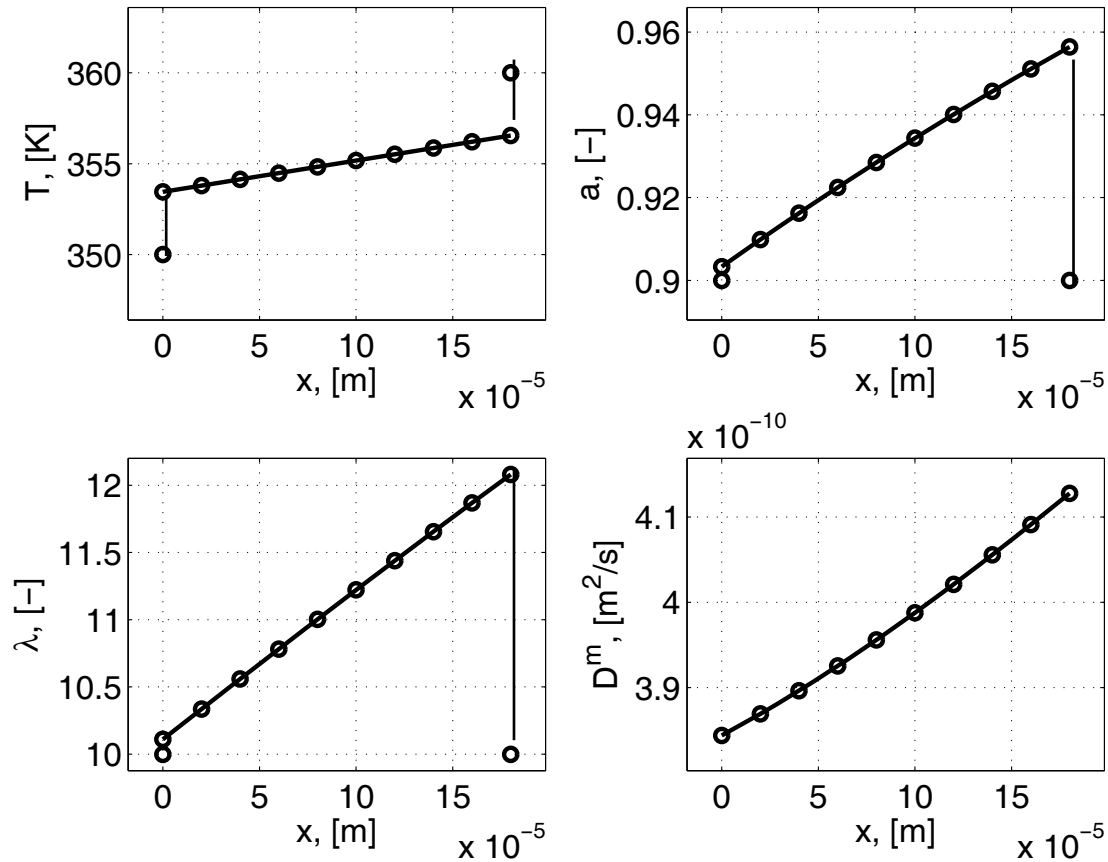
*Water flux is zero

Water content, diffusion coefficient

What happens when $\Delta\mu_T = 0$?

The flux of water due to a thermal force given by 10 K is 1×10^{-6} mol/m² s (zero chemical force)

THERMO-OSMOSIS



Heat fluxes and membrane temperatures following a water flux

	Side a $T = 350 \text{ K}$	Membrane Side a	Membrane Side c	Side c
Gas activity	0.70	0.99 (0.93)	0.64 (0.51)	0.50
Water content	5.3	13.9 (10.8)	4.6 (3.5)	3.4
Heat flux	14862/8605	14863 /8606	14863/ 8606	14861 /8604
Temperature	350	335.1 (341.4)	321.8 (333.7)	306.9 (325.1)
$D^m \text{ (m}^2\text{/s)}$		2.7 (3.0) 10^{-10}	2.5 (4.6) 10^{-10}	

The set water flux: $1.9 \times 10^{-5} \text{ mol/m}^2 \text{ s}$.

Blue numbers: Calculations using zero coupling coefficients

Observations of practical significance

- A temperature gradient can enhance or counteract the osmotic effect.
- The sign of the effect is decided by the nature of the membrane and thus the coupling coefficient
- If heat is transferred along with the solvent, an enhancement can be expected in the direction of the thermal force.

Summary

- A systematic description of coupled transports of heat and mass across heterogeneous systems is feasible with non-equilibrium thermodynamics
- The coupling coefficient for heat and mass transfer at interfaces cannot be neglected in a thermodynamically consistent model
- A thermal force may enhance/ counteract a mass flux through a membrane that is not inert
- Neglect of coupling coefficients gives large errors in the heat fluxes out of the membrane

Exercise

1. Calculate the ideal work obtainable by mixing 1 mole of water into an excess of sea water at 293 K. Sea water has 54.9 kmol/ m³ water and 0.6 kmol/m³ salt (NaCl).
2. Where do you expect to find the largest dissipation of energy in a pressure retarded osmosis cell?