

# Non-Equilibrium Thermodynamics: Foundations and Applications.

## Lecture 4: Transport of heat and mass

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**<http://www.chem.ntnu.no/nonequilibrium-thermodynamics/>**

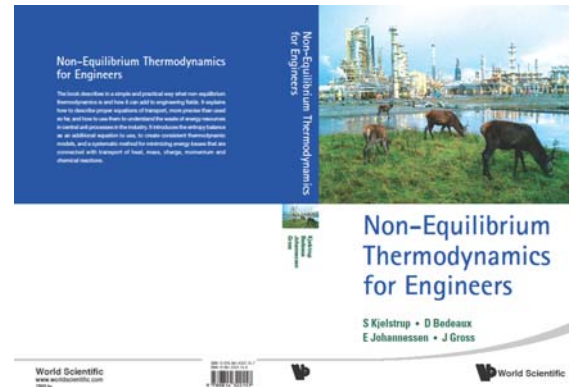
# Non-Equilibrium Thermodynamics: Foundations and Applications

	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

## Lecture 4. Transport of heat and mass

### Chapter 4.3



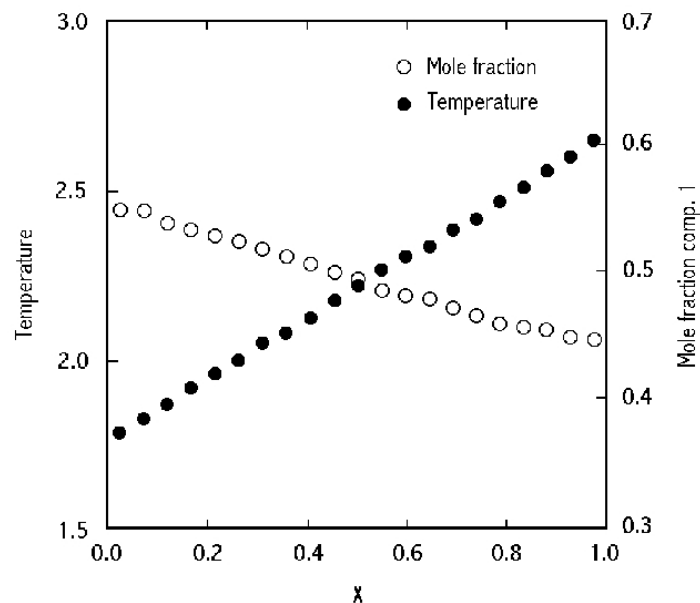
### Chapter 8



### Exercise 4

# Your working procedure

1. The entropy production
2. The fluxes
3. The coefficients
4. Separation technology / or
5. Mechanical work from thermal energy



A heat flux across a box,  
is able to maintain separation  
in a mixture

# Lost work by heat transport

- Heat transport along the x-axis. Cross-sectional area:  $\Omega$
- The lost work is the work that could have been obtained from a Carnot machine

$$\frac{dS_{irr}}{dt} = \Omega \int_L \sigma(x) dx = \Omega \int_L J'_q \frac{\partial}{\partial x} \left[ \frac{1}{T} \right] dx$$

*Stationary state:*

$$\frac{dS_{irr}}{dt} = \Omega J'_q \int_L \frac{\partial}{\partial x} \left[ \frac{1}{T} \right] dx = \Omega \frac{dQ}{dt} \left[ \frac{1}{T_c} - \frac{1}{T_h} \right]$$

$$w_{lost} = \eta_I \Omega \frac{T_0}{T_c} \frac{dQ}{dt} \qquad \eta_I = \frac{T_h - T_c}{T_h}$$

Can we recover some of this loss?

Answer: By conducting heat through a binary mixture:

## The entropy production of a mixture in contact with two thermal reservoirs

The thermal potential difference of the reservoirs separated by  $dx$

$$\sigma = J'_q \frac{d}{dx} \left( \frac{1}{T} \right) + J_1 \left( -\frac{1}{T} \frac{d}{dx} \mu_1 \right)$$

The measurable heat flux does not depend on the frame of reference

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

# The coupled flux equations

$$J'_q = L_{qq} \frac{\partial}{\partial x} \left( \frac{1}{T} \right) + L_{q\mu} \left( -\frac{1}{T} \frac{\partial \mu_{1,T}}{\partial x} \right)$$

$$J_1 = L_{\mu q} \frac{\partial}{\partial x} \left( \frac{1}{T} \right) + L_{\mu\mu} \left( -\frac{1}{T} \frac{\partial \mu_{1,T}}{\partial x} \right)$$

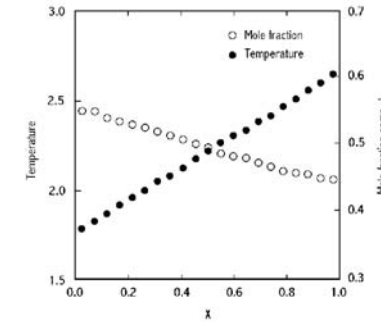
Relation to Fick's and Fourier's law:

$$J_1 = -D \frac{\partial c_1}{\partial x} = -L_{\mu\mu} \frac{1}{T} \frac{\partial \mu_{1,T}}{\partial x} = -L_{\mu\mu} \frac{R}{c_1} \left( \frac{\partial \mu_{1,T}}{\partial c_1} \right) \frac{\partial c_1}{\partial x} \quad J'_q = L_{qq} \frac{\partial}{\partial x} \left( \frac{1}{T} \right) = -\frac{L_{qq}}{T^2} \frac{\partial T}{\partial x} = -\lambda \frac{\partial T}{\partial x}$$

The Onsager relation  $L_{\mu q} = L_{q\mu}$

is linking the Soret effect and the Dufour effect

# The heat flux causes separation



- Diffusive and convective heat transfer are superimposed:

$$J'_q = L_{qq} \frac{\partial}{\partial x} \left( \frac{1}{T} \right) + L_{q\mu} \left( -\frac{1}{T} \frac{\partial \mu_1}{\partial x} \right)$$

$$J_1 = L_{\mu q} \frac{\partial}{\partial x} \left( \frac{1}{T} \right) + L_{\mu\mu} \left( -\frac{1}{T} \frac{\partial \mu_1}{\partial x} \right)$$

$$J'_q = - \left( L_{qq} - \frac{L_{\mu q} L_{q\mu}}{L_{\mu\mu}} \right) \frac{1}{T^2} \frac{\partial T}{\partial x} + \frac{L_{q\mu}}{L_{\mu\mu}} J_1$$

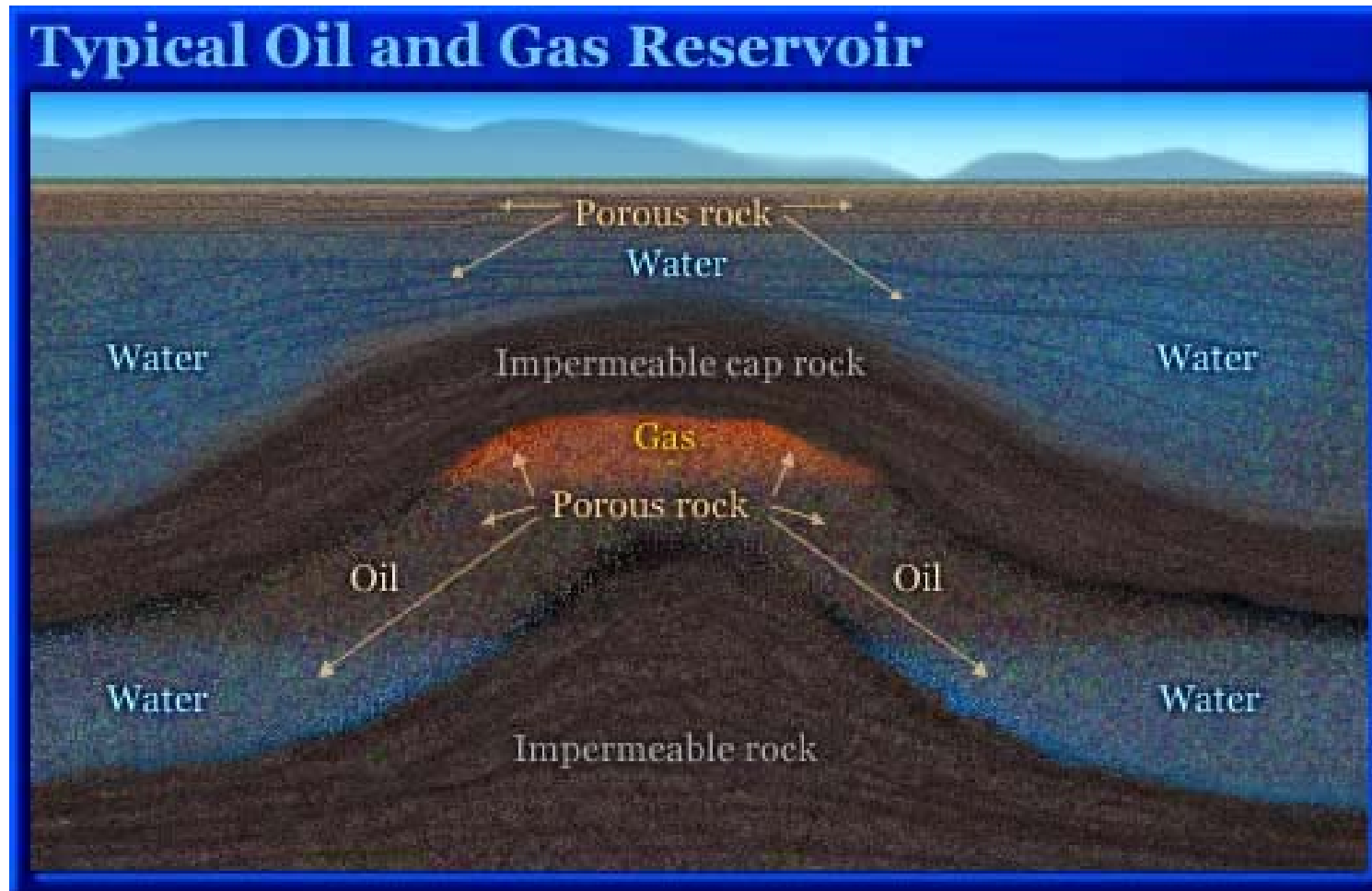
Coupling reduces the thermal conductivity

Coupling gives a convective heat current

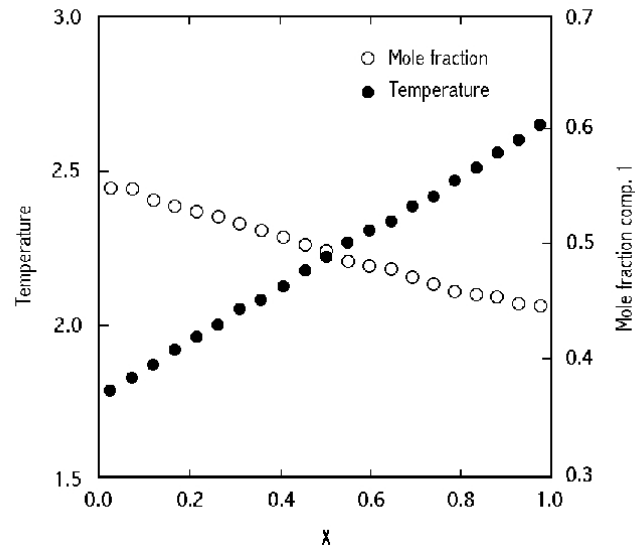
Each component takes part in the heat transport!



Can a temperature gradient explain separation of hydrocarbons in oil reservoirs?



# Soret equilibrium ( $J_1 = 0$ )



Defines the thermal diffusion coefficient

$$J'_q = L_{qq} \frac{\partial}{\partial x} \left( \frac{1}{T} \right) + L_{q\mu} \left( -\frac{1}{T} \frac{\partial \mu_1}{\partial x} \right)$$

$$J_1 = 0 = L_{\mu q} \frac{\partial}{\partial x} \left( \frac{1}{T} \right) + L_{\mu\mu} \left( -\frac{1}{T} \frac{\partial \mu_1}{\partial x} \right) \equiv -D_T c_1 \frac{\partial T}{\partial x} - D_{1,2} \frac{\partial c_1}{\partial x}$$

$$d\mu_1 = -\frac{L_{\mu q}}{L_{\mu\mu}} \frac{1}{T} dT$$

$$s_T = -\left( \frac{\Delta c_1}{c_1 \Delta T} \right)_{J_1=0} = \frac{D_T}{D_{1,2}}$$

Diffusion coefficient

The Soret coefficient, a measure for the separation

Typical value:  $10^{-3} \text{ K}^{-1}$  (Wiegand, 2004)

# The Dufour effect

Defining the heat of transfer  
("transference coefficient of heat")

$$J'_q = L_{qq} \frac{\partial}{\partial x} \left( \frac{1}{T} \right) + L_{q\mu} \left( -\frac{1}{T} \frac{\partial \mu_{1,T}}{\partial x} \right)$$

$$J_1 = L_{\mu q} \frac{\partial}{\partial x} \left( \frac{1}{T} \right) + L_{\mu\mu} \left( -\frac{1}{T} \frac{\partial \mu_{1,T}}{\partial x} \right)$$

$$q_1^* = \left[ \frac{J'_q}{J_1} \right]_{dT=0} = \frac{L_{q\mu}}{L_{\mu\mu}}$$

Work by mixing / demixing:

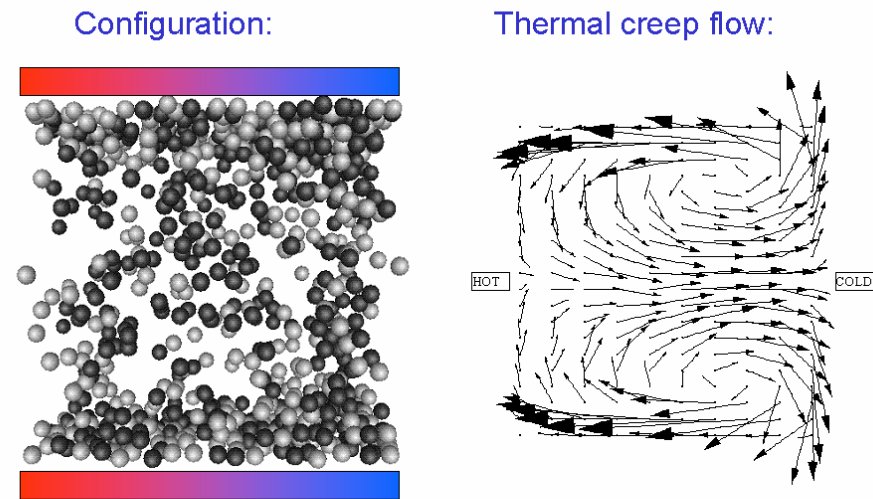
$$\int_L \frac{1}{T} \frac{\partial \mu_1}{\partial x} dx = \int_L \left[ q_1^* \frac{\partial}{\partial x} \left( \frac{1}{T} \right) - \frac{1}{L_{\mu\mu}} J_1 \right] dx$$

Useful work can be  
obtained from the  
gradient in temperature

We used the Onsager relation

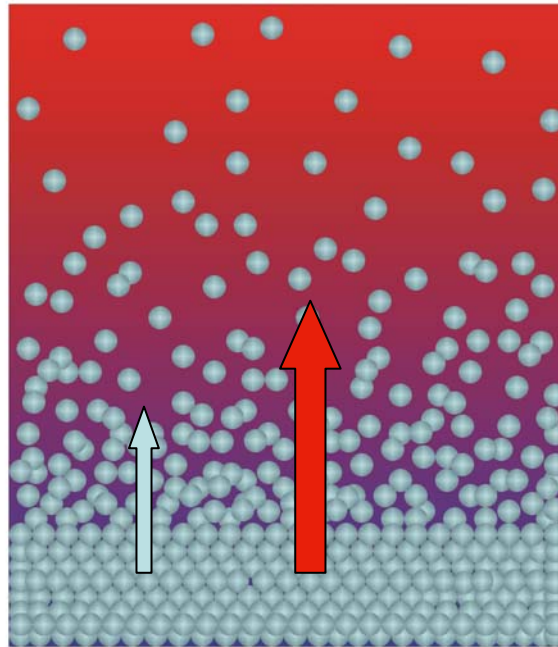
Frictional loss during (de)mixing

# A fluid in a pore with a temperature gradient<sup>1</sup>

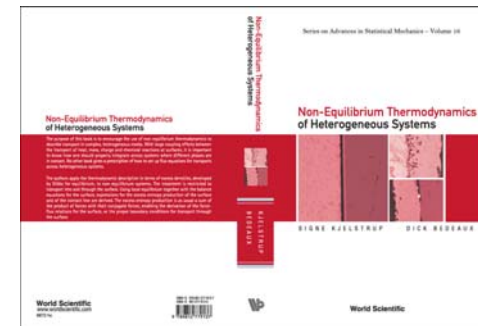


1. I. Wold and B. Hafskjold,  
Nonequilibrium molecular dynamics simulations  
of coupled heat- and mass transport in binary fluid mixtures in pores,  
Int. J. Thermophys. 20 (1999) 847 - 856

# Evaporation of one component

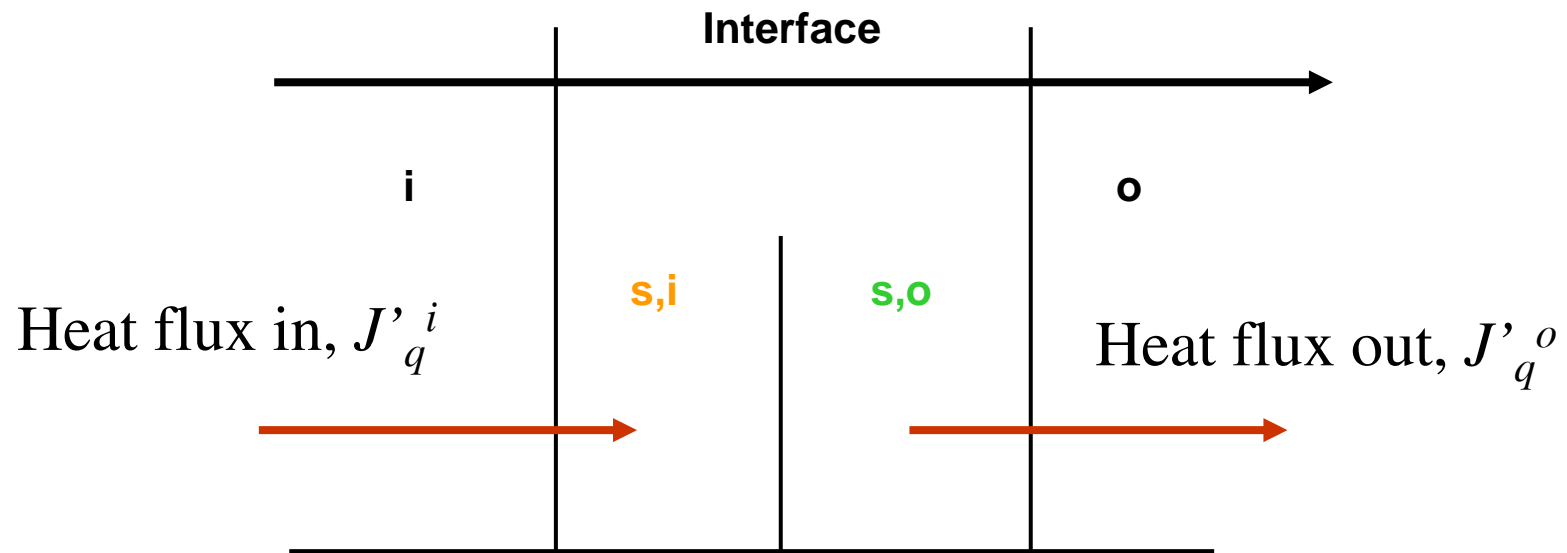


How can we describe transport through the interface?

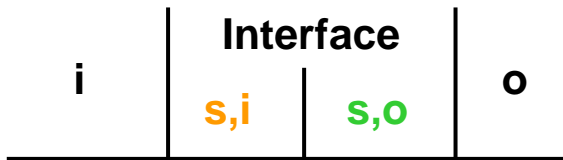


# Notation for interface transport

Constant mass flux,  $J_m$



## Equations of transport from the entropy production



$$\sigma^s = J_q^i \Delta_{i,s} \frac{1}{T} + J_q^o \Delta_{s,o} \frac{1}{T} + J_m^i \left( -\frac{1}{T^s} \Delta_{i,s} \mu_{m,T} (T^s) \right) + J_m^o \left( -\frac{1}{T^s} \Delta_{s,o} \mu_{m,T} (T^s) \right)$$

### Linear flux-forces relations for the two sides of the interface

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

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

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

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

Stationary state transport *across* the interface:

Alternative sets

$$\begin{aligned} \Delta_{i,o} \frac{1}{T} &= r_{qq}^s J_q^i + r_{qm}^{s,l} J_m & \Delta_{i,o} \frac{1}{T} &= r_{qq}^s J_q^{i,o} + r_{qm}^{s,r} J_m \\ -\frac{1}{T^o} \Delta_{i,o} \mu_{m,T} (T^o) &= r_{mq}^{s,l} J_q^i + r_{mm}^{s,l} J_m & -\frac{1}{T^i} \Delta_{i,o} \mu_{m,T} (T^i) &= r_{mq}^{s,r} J_q^{i,o} + r_{mm}^{s,r} J_m \\ J_m^i &= J_m^o = J_m, & J_q^i + J_m H^i &= J_q^{i,o} + J_m H^o \end{aligned}$$

Surface heats of transfer, definitions:

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

But the surface heats of transfer are related!

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

Large Dufour effect when the enthalpy of evaporation is significant!



# Summary

- The transport phenomena are described by the fluxes and forces in the entropy production
- The origin of de-mixing work is the heat of transfer
- This coupling coefficient is small in most homogeneous phases. It may be significant for phase transitions
- We have studied a two-component one-phase system. Multicomponent systems follow the same pattern

## From Exercise 4.

A cylindrical container of length 5 mm is filled with an aqueous solution of KCl,  $c_{KCl} = 0.01 \text{ kmol m}^{-3}$ . The temperature on the left-hand side, l, is 20 °C, and on the right-hand side, r, 30 °C. In the stationary state a difference in concentration is established between the two sides,  $c_{KCl,r} - c_{KCl,l} = \Delta c_{KCl} = -1.25 \cdot 10^{-4} \text{ kmol m}^{-3}$ . The average Fick's diffusion coefficient for KCl in water is  $D = 1.9 \cdot 10^{-9} \text{ m}^2\text{s}^{-1}$ .

- a) Calculate the Soret coefficient,  $s_T$ , and the heat of transfer,  $q^*$  (use the mean temperature), for KCl in the solution.
- b) Calculate the flux of KCl at the starting time, when  $\Delta c_{KCl} = 0$ .