

# Non-Equilibrium Thermodynamics: Foundations and Applications.

## Lecture 2. Entropy production for a homogeneous phase

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

# Non-Equilibrium Thermodynamics: Foundations and Applications

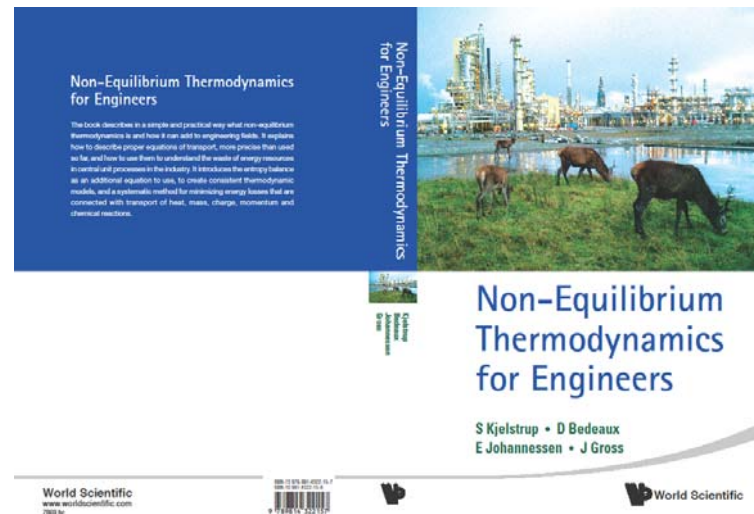
	Tuesday, Sept. 7	Wednesday, Sept. 8	Thursday, Sept.9	Friday, Sept.10
9:00-10:30	Why non-equilibrium thermodynamics?	Transport of heat and mass	Transport of heat and charge	Entropy production minimization theory
11:00-12:30	Entropy production for a homogeneous phase	Multi-component heat and mass diffusion	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 2. Entropy production for a homogeneous phase

”The heart of the theory”

Text: Chapter 3

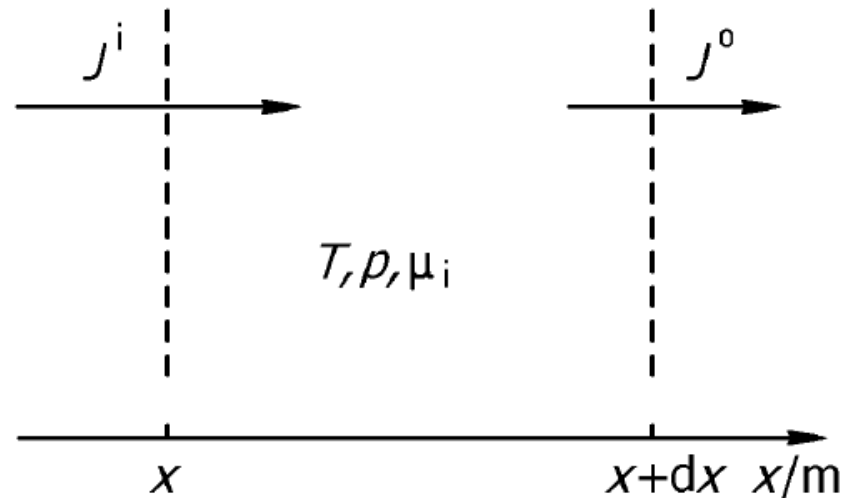


Exercise 2

# Finding the entropy production

We always combine:

1. Gibbs equation,
2. the first law
3. and mass balances



The volume element  
is at rest

# Gibbs equation for an open system

$$dU = TdS - pdV + \sum_{j=1}^n \mu_j dN_j$$

**We need a local formulation, so we introduce  $U=uV$ ,  $S=sV$ ,  $N_j=c_j V$**

$$Vdu + udV = T(Vds + sdV) - pdV + \sum \mu_j (c_j dV + Vdc_j)$$

$$V(du - Tds - \sum \mu_j dc_j) = (u - TS + p + \sum \mu_j c_j) dV$$

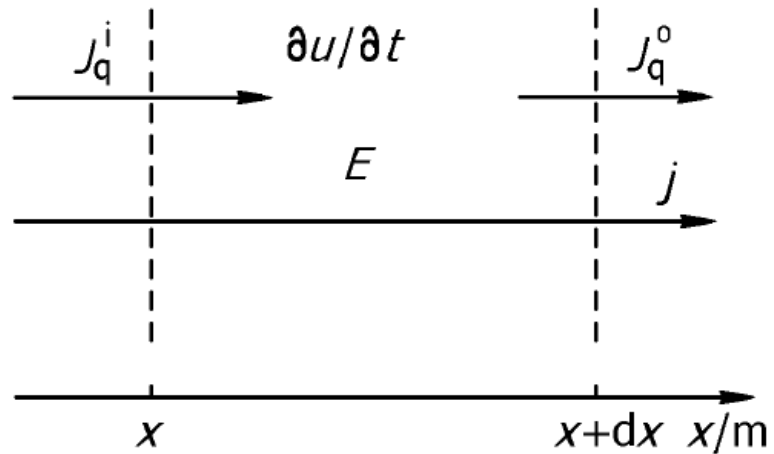
$$U = TS - pV + \sum \mu_j N_j \quad \times \frac{1}{V}$$

$$u = Ts - p + \sum \mu_j c_j$$

$$du = Tds + \sum \mu_j dc_j$$

$$\frac{ds}{dt} = \frac{1}{T} du - \frac{1}{T} \sum \mu_j \frac{dc_j}{dt}$$

# The first law of a system with transport of heat, mass and charge and chemical reaction\*



$$\frac{\partial u}{\partial t} = -\frac{\partial}{\partial x} J_q + E j$$

The total heat flux is the sum of the measurable heat flux and latent heat transported

$$J_q = J'_q + \sum_{j=1}^n H_j J_j$$

The measured emf and the gradient in electric potential

$$E = -\frac{\partial \phi}{\partial x}$$

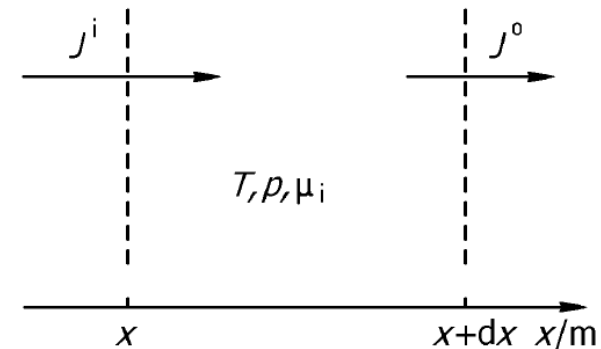
\*The system is in mechanical equilibrium

# Mass conservation

- The reaction rate  $r$  and the reaction Gibbs energy

$$\Delta_r G = \sum_j \nu_j \mu_j$$

$$\frac{\partial c_j}{\partial t} = -\frac{\partial}{\partial x} J_j \pm \nu_j r \quad \text{for } j = 1, \dots, n$$



- No charge accumulation

$$\frac{\partial z}{\partial t} = -\frac{\partial}{\partial x} j = 0$$

# Deriving the entropy production

$$\begin{aligned}
 \frac{\partial s}{\partial t} &= \frac{1}{T} \frac{\partial u}{\partial t} - \frac{1}{T} \sum \mu_j \frac{\partial c_j}{\partial t} = \\
 &= \frac{1}{T} \left[ -\frac{\partial}{\partial x} J_q + j \left( -\frac{\partial \phi}{\partial x} \right) \right] + \frac{1}{T} \sum \mu_j \left( -\frac{\partial J_j}{\partial x} \right) \\
 &= -\frac{\partial}{\partial x} \frac{J_q}{T} + J_q \frac{\partial}{\partial x} \left( \frac{1}{T} \right) - j \frac{1}{T} \frac{\partial \phi}{\partial x} + \sum \left[ \frac{\partial}{\partial x} \left( \frac{\mu_j J_j}{T} \right) - J_j \frac{\partial}{\partial x} \frac{\mu_j}{T} \right]
 \end{aligned}$$

$$\frac{\partial s}{\partial t} = -\frac{\partial}{\partial x} J_s + \sigma$$

**4 conjugate flux-force pairs**

$$\sigma = J_q \frac{\partial}{\partial x} \left( \frac{1}{T} \right) + j \left[ -\frac{1}{T} \frac{\partial \phi}{\partial x} \right] + \sum J_j \left[ -\frac{\partial}{\partial x} \frac{\mu_j}{T} \right] + r \left[ -\frac{\Delta G}{T} \right]$$

$$J_s = \frac{1}{T} [J_q - \mu_j J_j] = \frac{J_q'}{T} + S_j J_j$$

**Entropy flux**



# A practical problem:

- The total heat flux cannot be measured

$$J_q = J'_q + \sum_{j=1}^n H_j J_j$$

- We would like to replace the total heat flux by the measurable heat flux as a variable

$$\sigma = \left[ J'_q + \sum J_j H_j \right] \frac{\partial}{\partial x} \left( \frac{1}{T} \right) - j \frac{1}{T} \frac{\partial \phi}{\partial x} - \sum J_j \frac{\partial}{\partial x} \frac{\mu_j}{T} - r \frac{\Delta G}{T}$$

- In order to combine terms better we need the derivative of

$$\mu_j / T$$

# Mathematics for state functions:

## The differential of the chemical potential

gives the expression we introduce  
in the entropy production  
and obtain:

$$dG = -SdT + Vdp + \sum \mu_i dN_i$$

$$d\mu_j = -S_j dT + V_j dp + \sum \left( \frac{\partial \mu_j}{\partial N_i} \right)_{p,T,N_i} dN_i$$

$$d\mu_j = -S_j dT + V_j dp + d\mu_j^c$$

$$d \left[ \frac{\mu_j}{T} \right] = \frac{1}{T} \left( d\mu_{j,T} + \frac{d\mu_j}{dT} dT \right) + \mu_j d \left[ \frac{1}{T} \right]$$

$$= \frac{1}{T} (d\mu_{j,T} - S_j dT) + \mu_j d \left[ \frac{1}{T} \right]$$

$$\text{with } d\mu_{j,T} = V_j dp + d\mu_j^c = d\mu_j + S_j dT$$

$$\sigma = \left[ J'_q + \sum J_j H_j \right] \frac{\partial}{\partial x} \left( \frac{1}{T} \right) - j \frac{1}{T} \frac{\partial \phi}{\partial x} - \sum J_j \frac{\partial \mu_j}{\partial x} + \dots$$

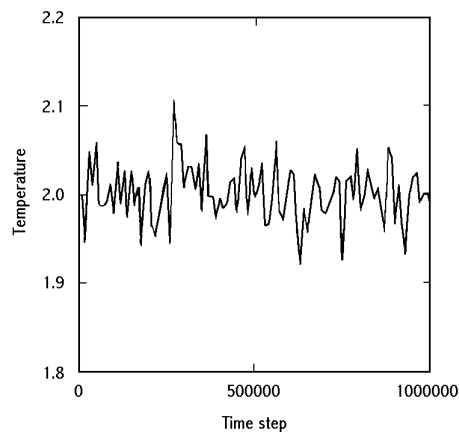
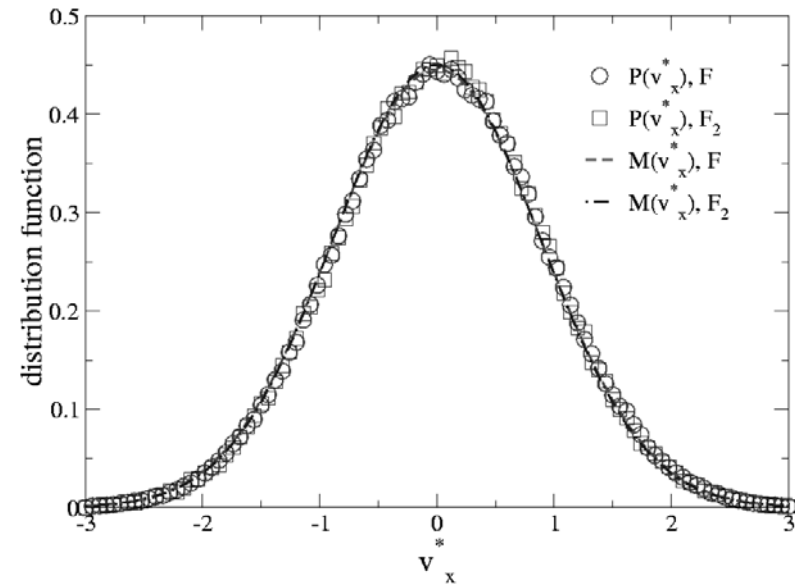
$$= \left[ J'_q + \sum J_j H_j \right] \frac{\partial}{\partial x} \left( \frac{1}{T} \right) - j \frac{1}{T} \frac{\partial \phi}{\partial x} - \sum J_j \left[ \frac{1}{T} \left( \frac{\partial \mu_{j,T}}{\partial x} - S_j \frac{\partial}{\partial x} T \right) + \mu_j \frac{\partial}{\partial x} \left[ \frac{1}{T} \right] \right] + \dots$$

$$= J'_q \frac{\partial}{\partial x} \left( \frac{1}{T} \right) + j \left( -\frac{1}{T} \frac{\partial \phi}{\partial x} \right) + \sum J_j \left[ -\frac{1}{T} \frac{\partial \mu_{j,T}}{\partial x} \right] + \dots$$

**This form can be related to experiments!**

# A basic assumption: Local equilibrium exists

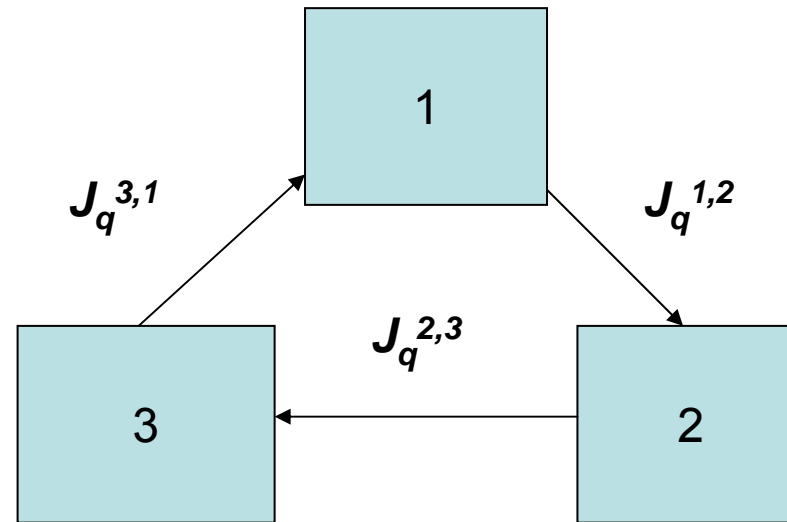
- There is local equilibrium in all volume elements
- Meaning: Molecular velocity distributions are nearly Maxwellian
- In this example, this is applies to a chemical reaction (2 fluorine atoms react to the molecule)



Temperature and concentration fluctuations are large

# Why we must use the entropy production to define dissipation

Consider an Example of three reservoirs with heat transport between them



The total entropy production is:

$$\begin{aligned} \frac{dS_{irr}}{dt} &= \frac{1}{T_1} \frac{dU_1}{dt} + \frac{1}{T_2} \frac{dU_2}{dt} + \frac{1}{T_3} \frac{dU_3}{dt} \\ &= J_q^{1,2} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right] + J_q^{2,3} \left[ \frac{1}{T_3} - \frac{1}{T_2} \right] + J_q^{3,1} \left[ \frac{1}{T_1} - \frac{1}{T_3} \right] \neq 0 \end{aligned}$$

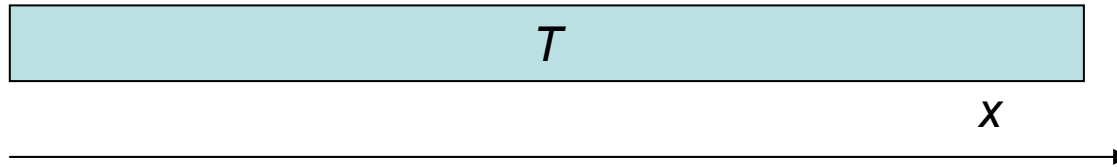
This *dissipation function* gives zero losses!  $\psi = T_1 \frac{dS_1}{dt} + T_2 \frac{dS_2}{dt} + T_3 \frac{dS_3}{dt} = 0$

# Understanding the entropy production as lost work

## Examples

- Charge transport
- Heat transport
- Mass transport
- Chemical reactions

# Lost work in electric conductors



$$\sigma = j \left[ -\frac{1}{T} \frac{\partial \phi}{\partial x} \right]$$

$$\text{Ohms law: } j = -\frac{1}{r} \frac{\partial \phi}{\partial x}$$

$$\sigma = \frac{1}{T} r j^2$$

$$\text{Joule heat: } r j^2 = \sigma T$$

*Resistivity*

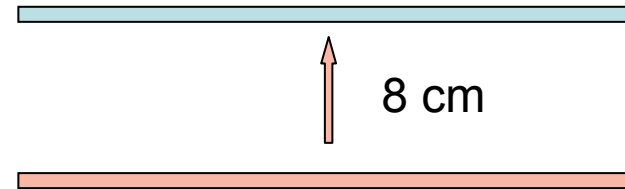
 Lost work at  $T$

Example:  $T = T_0 = 300 \text{ K}$   
 $r = 2 \cdot 10^{-6} \text{ ohm m}, j = 1 \cdot 10^4 \text{ A m}^{-2}$

$$\sigma = 0.67 \text{ J/K s m}^3$$

$$T_0 \sigma = 200 \text{ W/ m}^3$$

# Lost work by heat transport



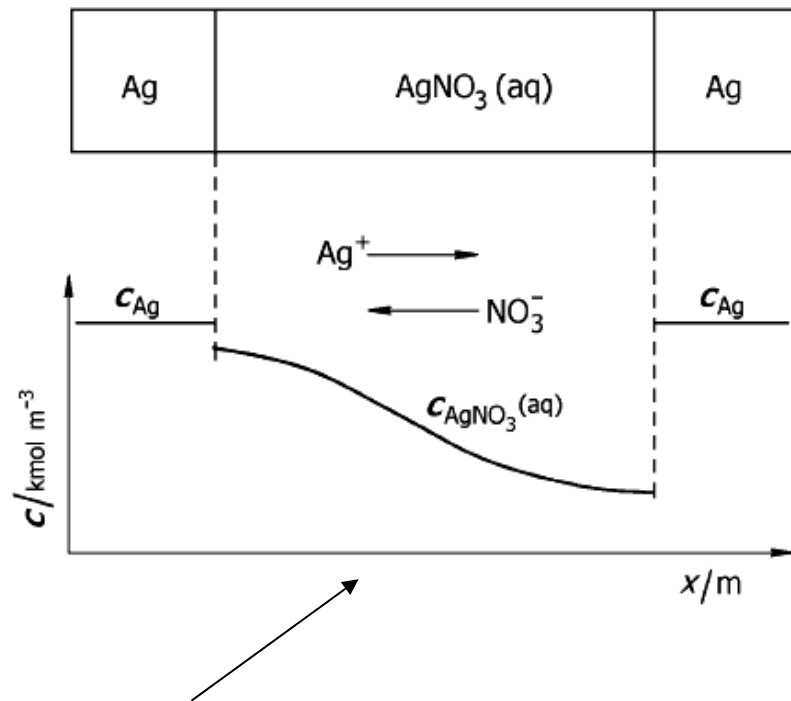
- Consider a heated pavement, area  $\Omega$ . A heating plate, 8 cm below, is turned on at 343 K when the snow starts to fall. What is the lost work per volume during heating?

Fourier's law for heat conduction is  $J'_q = -\lambda(dT/dx)$ . The entropy production is rather large:

$$\begin{aligned}\frac{1}{d} \int_0^d \sigma dx &= \frac{1}{d} \int_0^d J'_q \frac{\partial}{\partial x} \left( \frac{1}{T} \right) dx = -\lambda \frac{\Delta T}{d^2} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \\ &= -0.7 \frac{(-70)}{(0.08)^2} \left( \frac{1}{273} - \frac{1}{343} \right) = 5.7 \text{ W/K m}^3\end{aligned}$$

Lost work: 1,56 kW /m<sup>3</sup>

# Potential work, lost by diffusion



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

- The energy available for work in this concentration cell is represented by the concentration gradient of the salt.
- Diffusion will after some time make the system homogeneous.

## Example:

$$T = 300 \text{ K}, R = 8.31 \text{ J/K mol}, c = 1 \text{ kmol/m}^3$$

$$D = 10^{-9} \text{ m}^2/\text{s}, dc/dx = -10^3 \text{ mol m}^{-4}$$

$$\sigma = (-Ddc/dx)(-(R/c)dc/dx) = 10^{-5} \text{ J/s K m}^{-3}$$



# Lost work in chemical reactors

- All of the available energy is lost, unless the heat exchanged with the outside is made useful

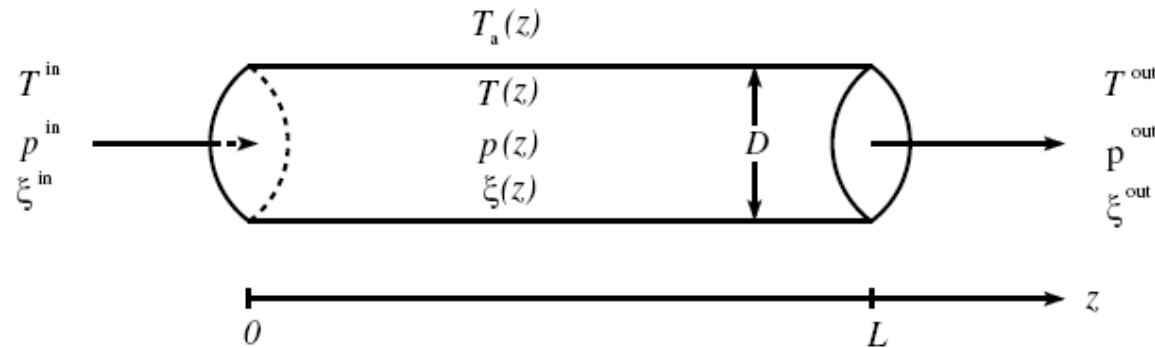


Figure 6.6: A tubular reactor.

**Total entropy production:**

$$\begin{aligned} \frac{dS_{irr}}{dt} &= S_{out} - S_{in} - \pi D \int_0^L \frac{J'_q}{T_a} dz \\ &= \int_0^L \left[ \Omega \rho_B \sum_j \left[ r_j \left( -\frac{\Delta_r G_j}{T} \right) \right] + \pi D J'_q \Delta \frac{1}{T} + \Omega v \left( -\frac{1}{T} \frac{dp}{dz} \right) \right] dz \end{aligned}$$

**Can be very large!**

**The engineering challenge**

# Properties of the entropy production (ep)

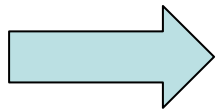
- **The ep determines conjugate flux-force pairs**
- **We find the form of ep without knowledge of the fluxes!**
- **The ep-value is independent of the frame of reference**
- **A change in one flux can lead to a change in a force not conjugate**
- **Equivalent forms of the ep exists. Other forms can be found, i.e. using the entropy flux;**

$$J_s = \frac{1}{T} \left( J_q - \sum_{j=1}^n \mu_j J_j \right) = \frac{1}{T} \left( J'_q + \sum_{j=1}^n S_j J_j \right)$$

- **The form to use depends on the application**

# Summary

1. The lost work can be studied in terms of fluxes and forces
2. The lost work is large in systems that transport heat or have chemical reactions.
3. The smaller the gradients and the rates are, the smaller is the lost work
4. When we want to accomplish a task, i.e. have a certain amount of heat exchanged, the question arises: Do we have a choice between paths with different entropy production?



*The answer to this question is discussed in Lectures 10,11*

$$\sigma = J_q \frac{\partial}{\partial x} \left( \frac{1}{T} \right) + j \left[ -\frac{1}{T} \frac{\partial \phi}{\partial x} \right] + \sum J_j \left[ -\frac{\partial \mu_j}{\partial x T} \right] + r \left[ -\frac{\Delta G}{T} \right]$$

## Exercise to Lecture 2

$$\sigma = J_q \frac{\partial}{\partial x} \left( \frac{1}{T} \right) + j \left( -\frac{1}{T} \frac{\partial \phi}{\partial x} \right) + \sum J_j \left[ -\frac{1}{T} \frac{\partial \mu_{j,T}}{\partial x} \right] + r \left( -\frac{\Delta_r G}{T} \right)$$

1. What is the conjugate force of the measurable heat flux?  
The total heat flux?
  - What is the conjugate force of the electric current density
  - What is the conjugate flux of the gradient  $-d(\mu/T)dx$
  
2. Describe the difference between the thermodynamic driving forces and the driving forces from the simple transport laws. Can the two descriptions be compatible?
  
3. Find the entropy production due to a heat flux through the bottom of an aluminium pan with boiling water. The surface of the heating plate is 150 °C. The bottom is 1,0 cm thick and its area is 3.0 dm<sup>2</sup>. The thermal conductivity is 237 W/K m.