

# Non-Equilibrium Thermodynamics: Foundations and Applications.

## Lecture 7: Transport of heat and charge

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

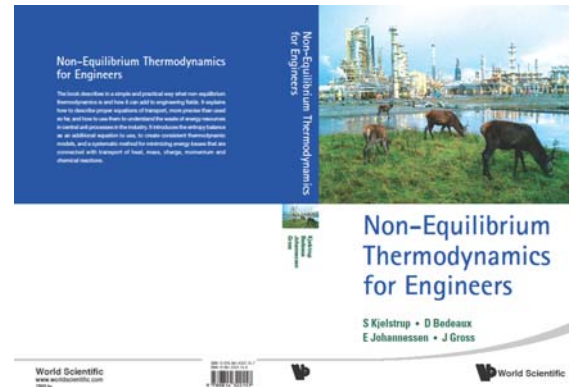
# Non-Equilibrium Thermodynamics: Foundations and Applications

	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

## 7. Transport of heat and charge

### Chapter 4.5



### Chapter 9



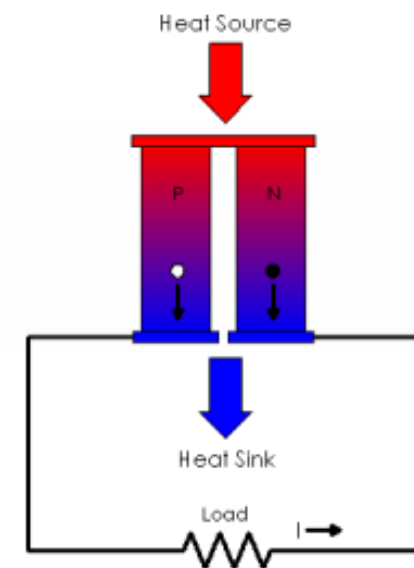
### Exercise

# Your working procedure

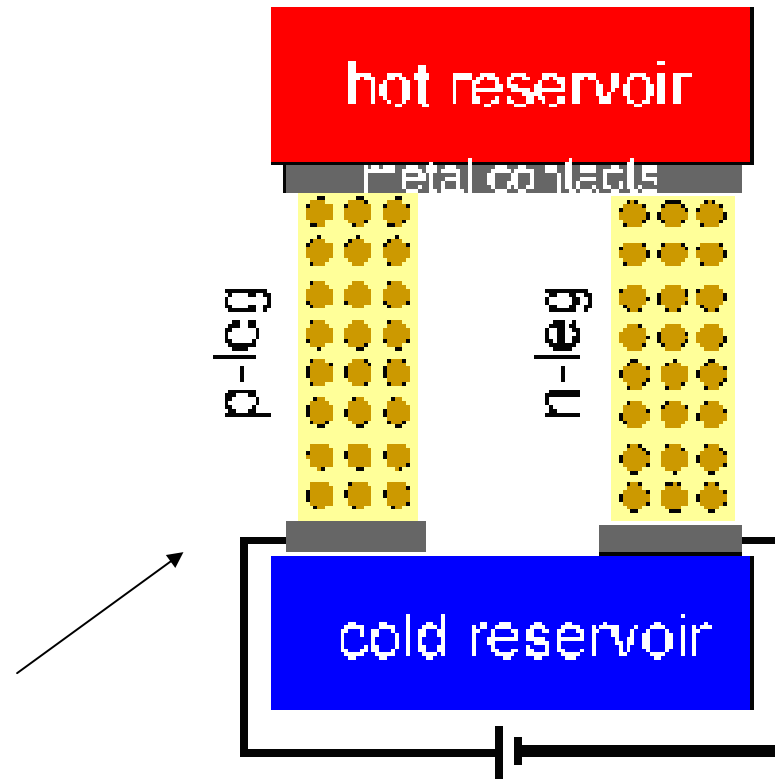
1. The entropy production
2. The fluxes
3. The coefficients
4. Electric work from thermal energy in an electrochemical cell
5. Adding work to provide cooling

BiTe ( $\text{Bi}_2\text{Te}_3$ )  
can be used around 400 °C

Thermocouple: Pt/Pt 10%Rh



# Potential work is lost by entropy production



*Two semiconductors  
In a temperature  
gradient*

- The energy available for work in the thermoelectric converted cell has its origin in the temperature gradient.
- Heat conduction will after some time make the system homogeneous, if heat reservoirs are not maintained

# The entropy production in the thermoelectric converter

The electric potential difference due to  $dT$  over a distance  $dx$

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

Heat flux in  $J/s \text{ m}^2$

Electric current density does also not depend on the frame of reference

# The coupled flux equations

$$J_q = L_{qq} \frac{\partial}{\partial x} \left( \frac{1}{T} \right) - L_{q\phi} \frac{1}{T} \frac{\partial \phi}{\partial x}$$

$$j = L_{\phi q} \frac{\partial}{\partial x} \left( \frac{1}{T} \right) - L_{\phi\phi} \frac{1}{T} \frac{\partial \phi}{\partial x}$$

Relations to Fourier's law

$$(J_q)_{dc=0} = -\lambda \frac{\partial T}{\partial x} = L_{qq} \frac{\partial}{\partial x} \left( \frac{1}{T} \right) = -\frac{L_{qq}}{T^2} \frac{\partial T}{\partial x}$$

$$\lambda(\bar{T}) = -\left( \frac{J_q}{\Delta T / \Delta x} \right)_{dc=0} = L_{qq} \frac{1}{\bar{T}^2}$$

and Ohm's law:

$$(j)_{dT=0} = -L_{\phi\phi} \frac{1}{T} \frac{\partial \phi}{\partial x}$$

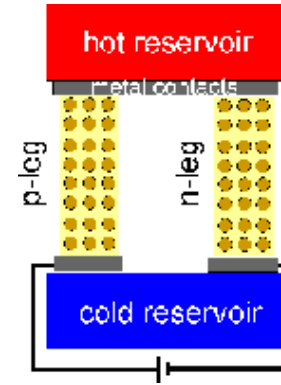
$$\frac{L_{\phi\phi}}{T} = -\left( \frac{j}{\Delta \phi / \Delta x} \right)_{dT=0}$$

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

Onsager relations are now linking the Peltier and Seebeck effects

# The heat flux

- Conduction and charge transfer are superimposed:



$$J_q = L_{qq} \frac{\partial}{\partial x} \left( \frac{1}{T} \right) - L_{q\phi} \frac{1}{T} \frac{\partial \phi}{\partial x}$$

$$j = L_{\phi q} \frac{\partial}{\partial x} \left( \frac{1}{T} \right) - L_{\phi\phi} \frac{1}{T} \frac{\partial \phi}{\partial x}$$

$$J_q = -\frac{1}{T^2} \left( L_{qq} - \frac{L_{q\phi} L_{\phi q}}{L_{\phi\phi}} \right) \frac{\partial T}{\partial x} + \frac{L_{q\phi}}{L_{\phi\phi}} j$$

Stationary state thermal conductivity  
< than thermal conductivity of  
Homogeneous conductor

Coupling means heat transport  
with the electric current

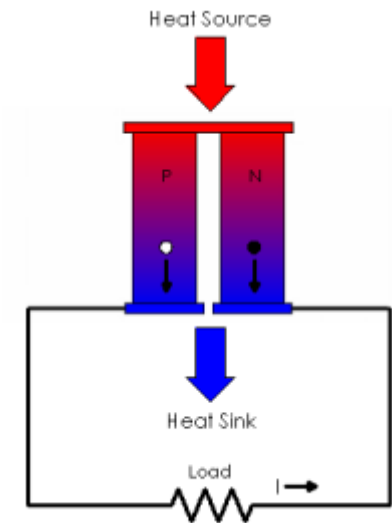
Defines the Peltier heat!



# The Peltier heat

$$J_q = -L_{qq} \frac{\partial}{\partial x} \left( \frac{1}{T} \right) - L_{q\phi} \frac{1}{T} \frac{\partial \phi}{\partial x}$$

$$j = -L_{\phi q} \frac{\partial}{\partial x} \left( \frac{1}{T} \right) - L_{\phi\phi} \frac{1}{T} \frac{\partial \phi}{\partial x}$$



Defining the Peltier heat:

$$\pi = \left[ \frac{J_q}{j} \right]_{dT=0} = \frac{L_{q\phi}}{L_{\phi\phi}}$$

Useful work from the temperature gradient

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

$$\Delta\phi = \int_L \frac{\partial \phi}{\partial x} dx = - \int_L \left[ \frac{\pi}{T} \frac{\partial T}{\partial x} - \frac{T}{L_{\phi\phi}} j \right] dx$$

We used the Onsager relation!

Ohmic potential drop across dx

# The Seebeck coefficient

$$\Delta\phi = \int_L \frac{\partial\phi}{\partial x} dx = - \int_L \left[ \frac{\pi}{T} \frac{\partial T}{\partial x} - \frac{T}{L_{\phi\phi}} j \right] dx$$

Useful work from the temperature gradient

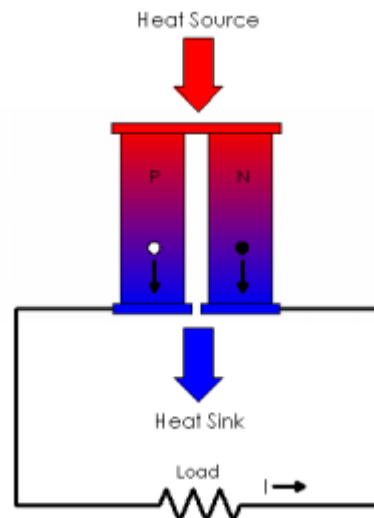
The Seebeck coefficient and the Peltier coefficient are related (Onsager relations)

$$\left( \frac{\Delta\phi}{\Delta T} \right)_{j=0} = - \left( \frac{\pi}{T} \right)_{dT=0}$$

Thermoelectric potential – for a semiconductor is a few mikrovolt per degree temperature difference

Seebeck coefficient: Relatively more easy to measure!

# Reversible heat transport in a conductor



$$J_q = -\frac{1}{T^2} \left( L_{qq} - \frac{L_{q\phi} L_{\phi q}}{L_{\phi\phi}} \right) \frac{\partial T}{\partial x} + \frac{L_{q\phi}}{L_{\phi\phi}} j$$

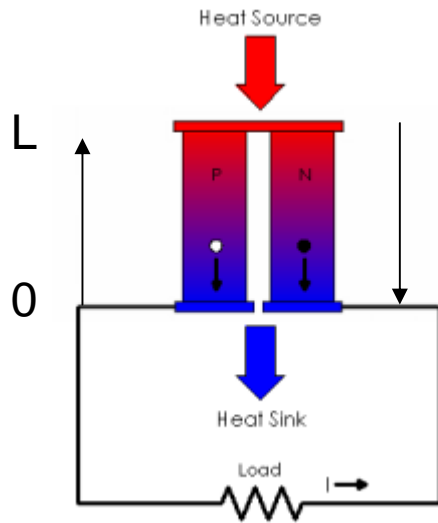
Heat carried with charge

Peltier heat

$$\left( \frac{J_q}{j} \right)_{dT=0} = \frac{L_{q\phi}}{L_{\phi\phi}} = \frac{\pi}{F} = \frac{1}{F} TS^*$$

Defines the transported entropy:  
Different for electrons, holes and ions!

# Thermoelectric power of a unit cell



$$\begin{aligned}\Delta\phi_{converter} &= \int_0^L \left( \frac{\partial\phi_p}{\partial x} \right) dx + \int_L^0 \left( \frac{\partial\phi_n}{\partial x} \right) dx = \int_0^L \left( \frac{\partial\phi_p}{\partial x} \right) dx - \int_0^L \left( \frac{\partial\phi_n}{\partial x} \right) dx \\ &= - \int_0^L \left( S_p^* \frac{1}{F} \frac{\partial T}{\partial x} - r_p j \right) dx - \int_L^0 \left( S_n^* \frac{1}{F} \frac{\partial T}{\partial x} - r_n j \right) dx \\ &= - \frac{1}{F} (S_p^* - S_n^*) \Delta T + (r_p + r_n) j \Delta x \\ \left[ \frac{\Delta\phi_{converter}}{\Delta T} \right]_{j=0} &= - \frac{1}{F} (S_p^* - S_n^*)\end{aligned}$$

Seebeck coefficient of a unit cell.  
 Several units make one module.  
 Larger effects in electrochemical cells?

# Are thermoelectric converters useful?



$$\pi = \left[ \frac{J_q}{j} \right]_{dT=0} = \frac{L_{q\phi}}{L_{\phi\phi}} = TS^*$$



The electric work from transported entropies

$$\left[ \frac{\Delta\phi_{converter}}{\Delta T} \right]_{j=0} = -\frac{1}{F} (S_p^* - S_n^*)$$

An Icelandic company is developing thermoelectric applications for harnessing geothermal power.

A converter with no moving parts.  
The thermocouple

# Cooling by thermoelectricity

- Thermoelectric coolers make use of the Peltier effect to transport heat, applying an electric current. The junction of materials cools down



# Summary

- The transports of heat and charge have been described by the fluxes and forces defined by the entropy production
- The origin of electric work in systems with transport of heat and charge is the coupling coefficient, or the Peltier heat (transported entropy)
- This coupling coefficient is not large in semiconductors
- We have studied simple thermoelectric converters. Reversible heat transport may be important in industry as well as in biology

# Exercise for Lecture 7

1. The temperature difference available in a casting area of a silicon producer is 300 K. What is the electric potential obtainable from a thermoelectric module with Seebeck coefficient  $3.82 \cdot 10^{-3}$  V/K? The module electric resistance is 1.8 ohm. How many modules are needed to run a fan which requires 5.9 W at 0.1 A?
2. What is the heat flux obtainable from one module, passing an electric current through the junction of 0.1 A at isothermal conditions?