Non-Equilibrium Thermodynamics for Engineers

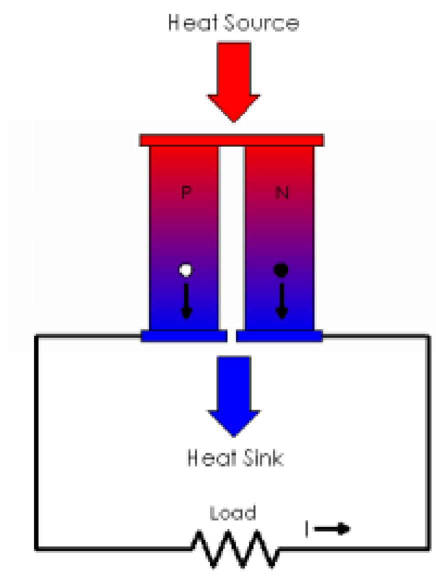
”Coupled transport of heat and charge”

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

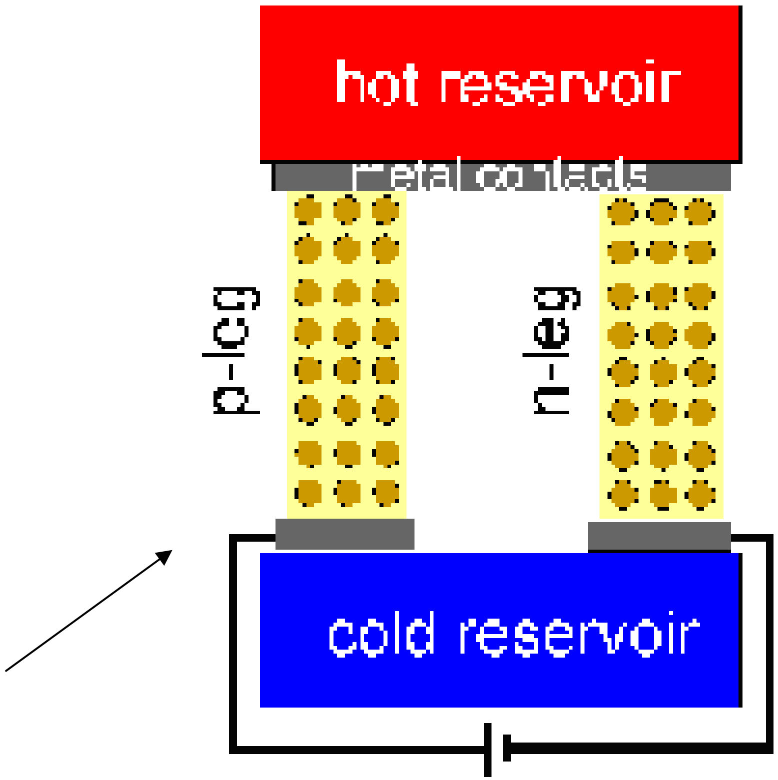
Lecture no. 6

Transport of heat and charge

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



Potential work can be lost by heat conduction in this cell



Two semiconductors
In a temperature
gradient

- The energy available for work in the thermoelectric converted cell lies in the temperature gradient.

- Conduction will after some time make the system homogeneous, if the heat reservoirs cannot be maintained

The entropy production of the thermoelectric converter

The electric potential difference between the two conductors over a distance d*x*

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

Heat is transported in J/s m^2. The walll is the frame of reference.

The electric current density does not depend on the frame of reference

The coupled flux equations

$$J_1 = L_{qq} \frac{\partial}{\partial x}\left(\frac{1}{T}\right) - L_{q\phi} \frac{1}{T} \frac{\partial \phi}{\partial x}$$

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

Relations to Fourier's and Ohm's law:

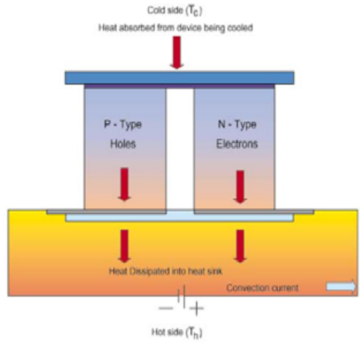
$$J_1 = -\lambda \frac{\partial T}{\partial x} = L_{qq} \frac{\partial}{\partial x}\left(\frac{1}{T}\right)$$

$$j = -L_{\phi\phi} \frac{1}{T} \frac{\partial \phi}{\partial x}$$

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

Onsager relations are linking Peltier's and Seebeck measurements

The heat flux



- Conduction and charge transfer are superimposed:

$$J_1 = L_{qq}\frac{\partial}{\partial x}\left(\frac{1}{T}\right) - L_{q\phi}\frac{1}{T}\frac{\partial \phi}{\partial x}$$

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

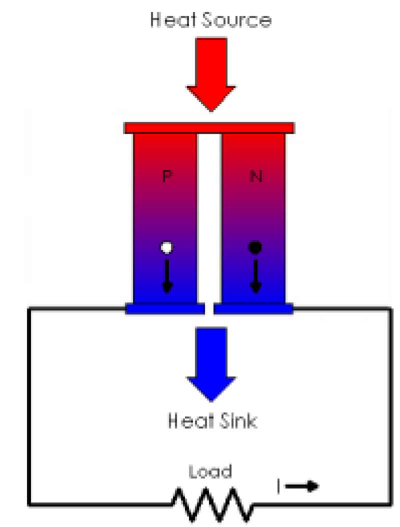
$$J_q = -\frac{1}{T^2}\left(L_{qq} - \frac{L_{q\phi}L_{\phi q}}{L_{\phi\phi}}\right)\frac{\partial T}{\partial x} + \frac{L_{q\phi}}{L_{\phi\phi}}\, j$$

Coupling reduces the thermal conductivity

Coupling gives heat transport with the electric current

Cooling or heating effect: Peltier showed that

The electric work



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

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

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!

Lecture no. 6

Ohmic potential drop

The electric work

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

Useful work from the gradient of chemical potential

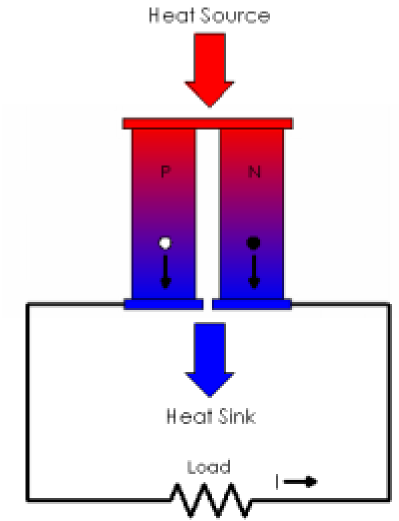
The Seebeck coefficient and the Peltier coefficient are related (Onsager relations)

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

The thermocell has a potential difference of a few mikrovolt per degree temperature difference

→ But the heat fluxes can be large!

How can we understand the reversible heat transport?



Are thermoelectric converters useful?

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

The electric work from the thermal sources:

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

An Icelandic company is developing thermoelectric applications for harnessing geothermal power, an abundant energy source in Iceland and many other regions of the world.

The Peltier heat is not large, but the converter has no moving parts.

Are thermoelectric converters useful?

- Thermoelectric coolers make use of the Peltier effect to transport heat

Summary

- The transport of heat and charge have been described by the fluxes and forces in the entropy production
- The origin of electric work in systems with transport of heat and charge is the coupling coefficent, or the Peltier coefficient
- The coupling coefficient is of the same order of magnitude as the other transport coefficients
- We have studied simple thermoelectric converters. Reversible heat transport may be important in industry as well as in biology