Non-Equilibrium Thermodynamics for Engineers

Lecture 3

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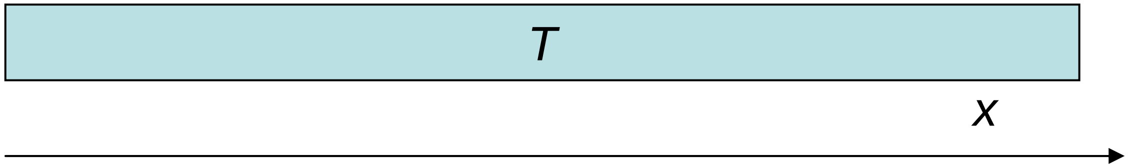
Explaining the entropy production as lost work

Examples

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

Lost work in electric conductors



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

Ohms law: $j = -\kappa\frac{\partial\phi}{\partial x}$

$\kappa = \frac{1}{r}$

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

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

Resistivity

⇒ Lost work at *T*

Lost work by heat transport, I

- Heat transport along the x-axis. Cross-sectional area: Ω

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

T_h

- The total entropy production and the Carnot efficiency

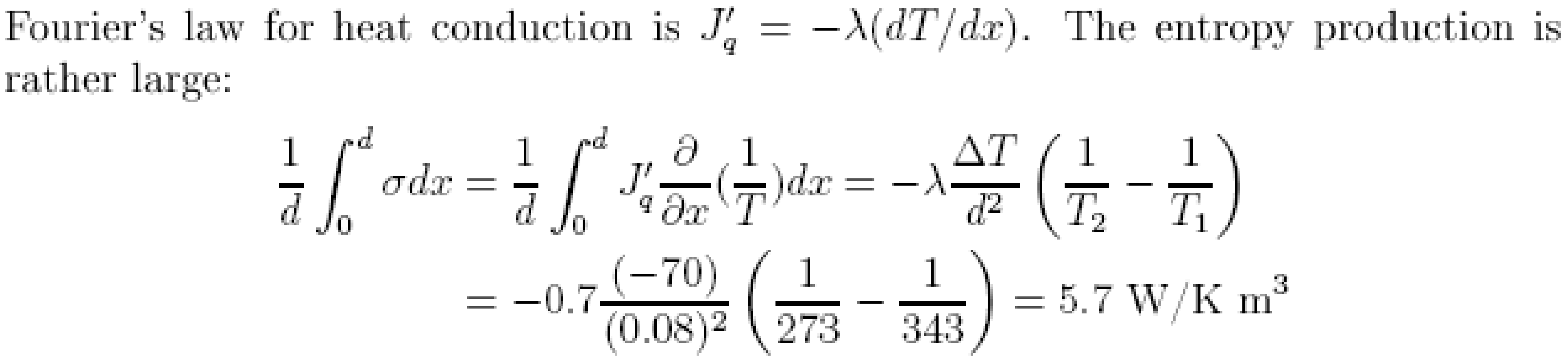
$$\begin{aligned}\frac{dS_{\text{irr}}}{dt} &= J'_q\Omega \int \frac{\partial}{\partial x}\left(\frac{1}{T(x)}\right)dx = J'_q\Omega \int_{T_h}^{T_c} \frac{\partial}{\partial T}\left(\frac{1}{T}\right)dT \\ &= \Omega\frac{dQ}{dt}\left(\frac{1}{T_c}-\frac{1}{T_h}\right) = \Omega\frac{dQ}{dt}\left(\frac{T_h-T_c}{T_hT_c}\right) = \Omega\frac{\eta_I}{T_c}\frac{dQ}{dt}\end{aligned}$$

The lost work is identical to work that can be obtained in a Carnot machine (which is reversible).

$$w_{lost} = T_c\eta_I\Omega\frac{dQ}{dt}$$

Lost work by heat transport, II

- **Consider a heated pavement, area Ω. The heating plate, 8 cm below, is turned on to melt snow when *T* is 10 K below melting.**
- **What is the lost work during heating?**



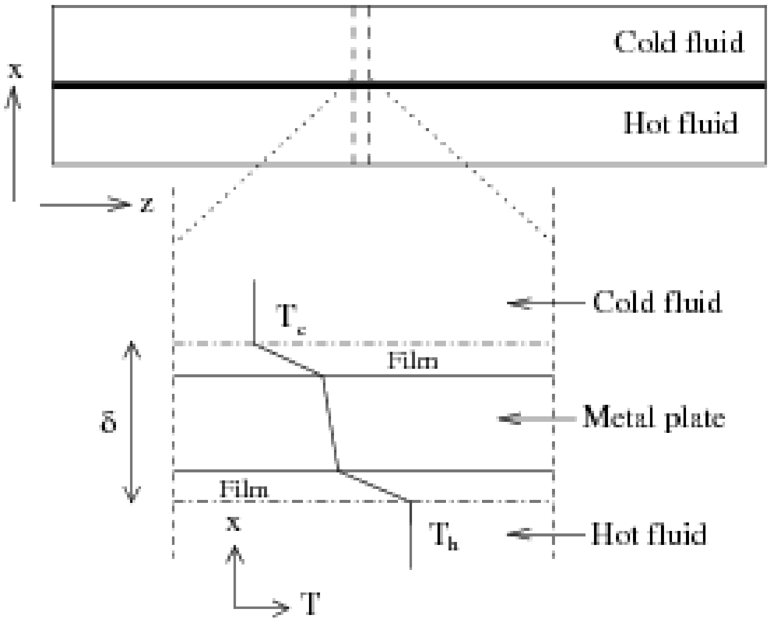
Fourier's law for heat conduction is $J'_q = -\lambda(dT/dx)$. The entropy production is rather large:

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

Lost work in a heat exchanger

Total entropy production from local heat transport at *x* and *z*

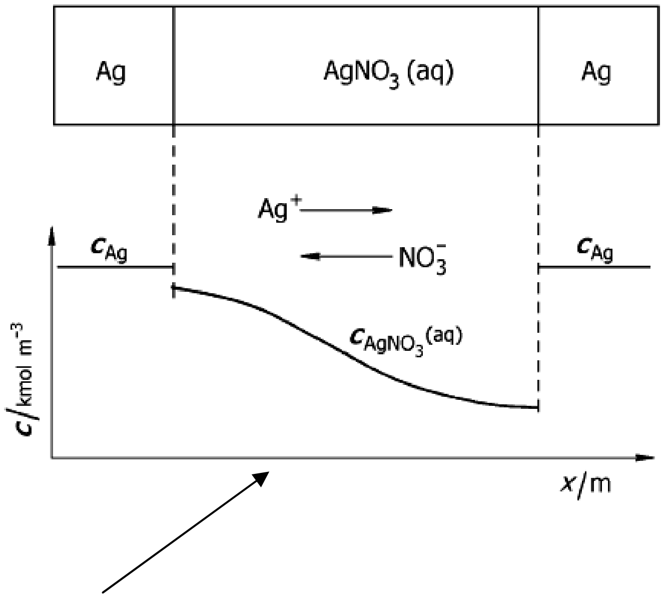
$$\frac{dS_{\text{irr}}}{dt} = \Delta y \int_0^L \int_0^\delta \sigma(x,z)\,dx\,dz = \int_0^L \sigma(z)\,dz$$
$$= \Delta y \int_0^L l_{qq}\left(T_h(z)\right)\left[\Delta\left(\frac{1}{T}\right)\right]^2 dz.$$



Total entropy production from the total entropy balance

$$\frac{dS_{\text{irr}}}{dt} = F\,S_{\text{out}} - F\,S_{\text{in}} - \Delta y \int_0^L \frac{J_q'(z)}{T_c(z)}\,dz$$

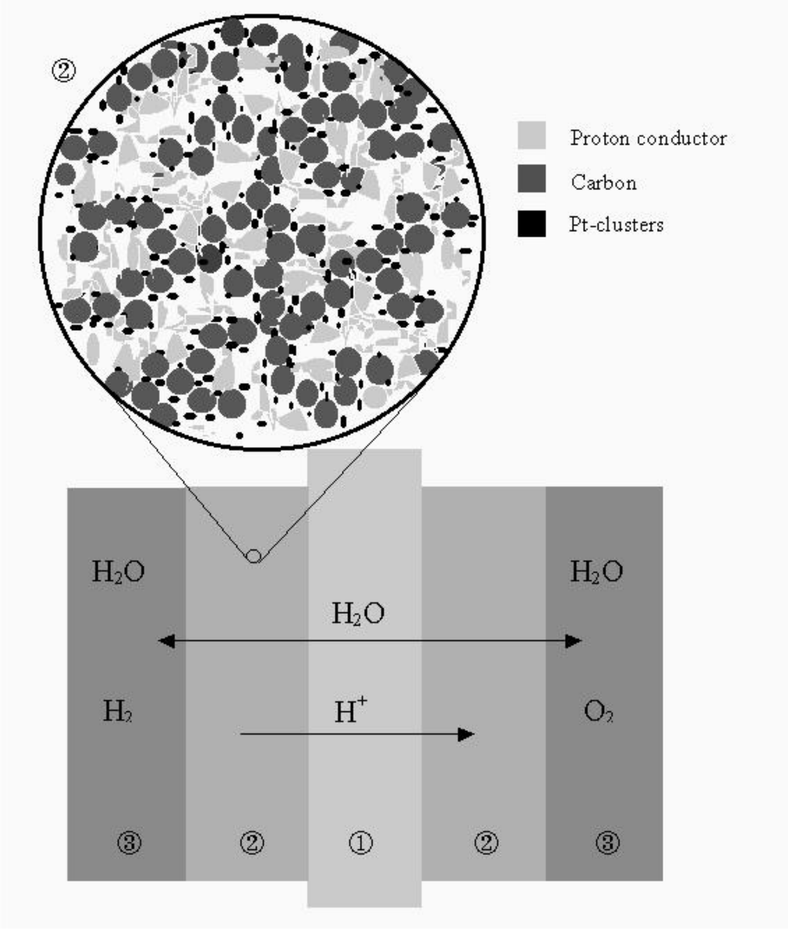
Potential work can be lost by diffusion

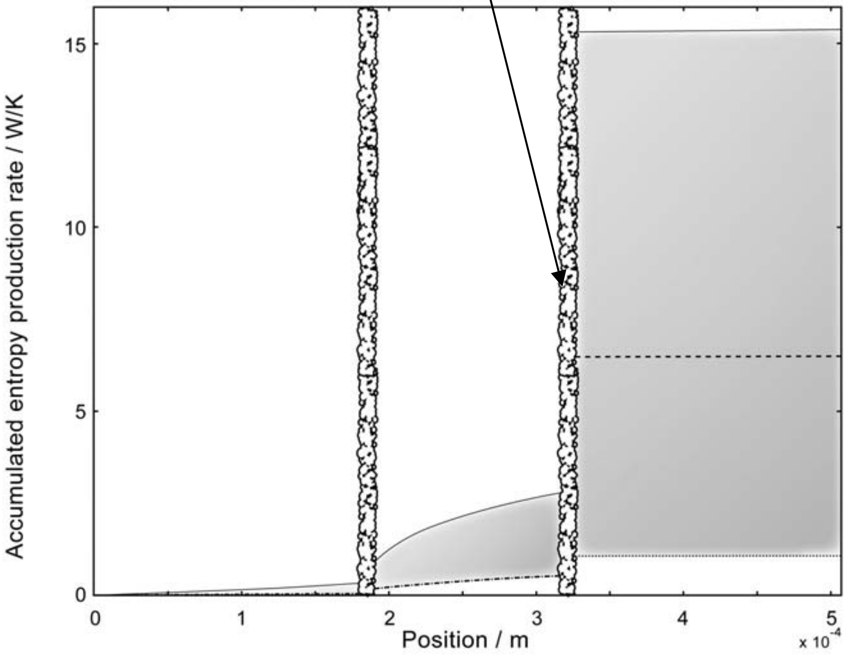


Two electrodes of silver in a non-uniform solution of silver nitrate

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

The accumulated entropy production, as a function of position across the polymer electrolyte fuel cell





Largest loss from the cathode overpotential

- **Results are shows for current densities: 500, 2500 and 5000 A/m^2**

Lost work in chemical reactors

- All of the energy in the chemical reaction is lost, unless the heat exchange with the outside is made useful (exothermic reactions)

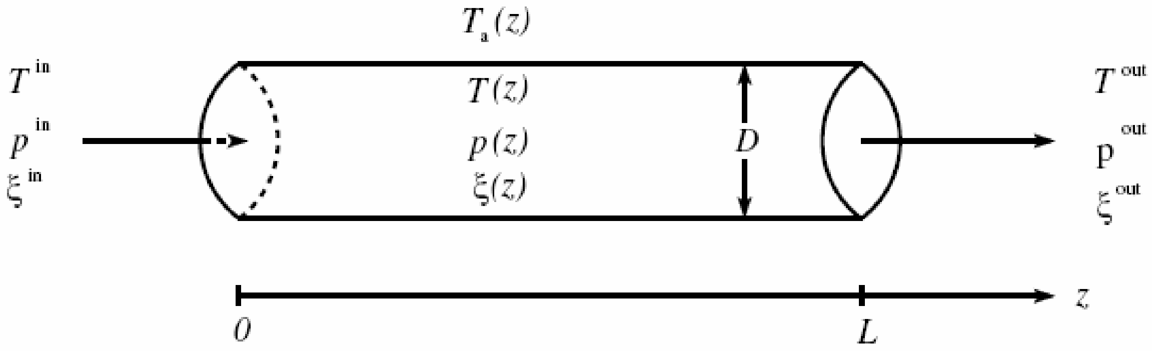
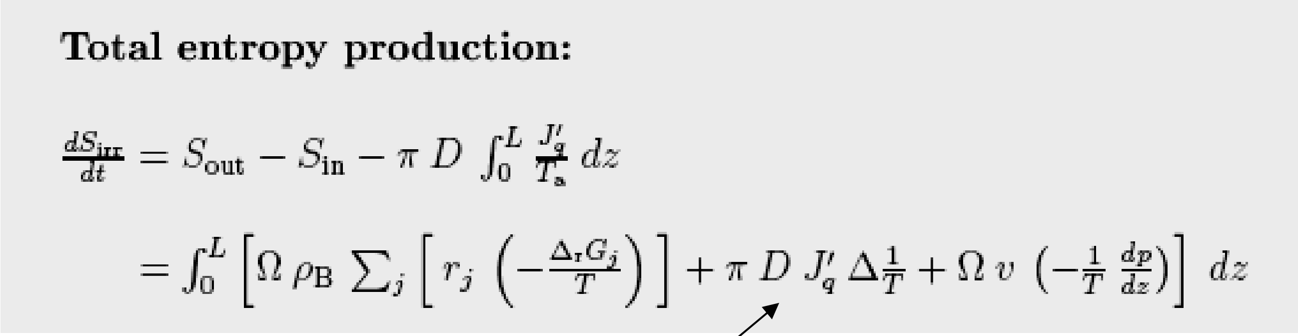


Figure 6.6: A tubular reactor.



Total entropy production:

$$\frac{dS_{\text{irr}}}{dt} = S_{\text{out}} - S_{\text{in}} - \pi\, D \int_0^L \frac{J_q'}{T_a}\, dz$$

$$= \int_0^L \left[\Omega\, \rho_{\text{B}} \sum_j \left[r_j \left(-\frac{\Delta_r G_j}{T} \right) \right] + \pi\, D\, J_q'\, \Delta \frac{1}{T} + \Omega\, v\, \left(-\frac{1}{T}\frac{dp}{dz} \right) \right] dz$$

The engineering challenge

Summary

1. The lost work can studied using the entropy production
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: Can we choose between paths with different entropy production?

The answer to this question is discussed in Ch.6