3.4 Calculation of ΔS for irreversible change of state

As already stated above the change of entropy for an irreversible change of state can be calculated for a reversible substitute since entropy is a state function and does not depend on the path from one state to the other. Here we will discuss two examples:

- The adjustment of the thermodynamic equilibrium between two identical metal blocks, but with different temperatures. So we have to calculate ΔS when two blocks of the same metal are contacted ($m_1 = m_2$, $C_{p,1} = C_{p,2}$, but $T_1 \neq T_2$). As a reversible substitute we split up the system into two subsystems

  $$\begin{aligned} \Delta S =& \int_{T_1}^{T_f} \frac{C_p}{T} dT + \int_{T_2}^{T_f} \frac{C_p}{T} dT \quad \text{with} \quad T_f = \frac{T_1 + T_2}{2} \\ \Delta S =& C_p \ln \left(\frac{(T_1 + T_2)^2}{4 T_1 T_2} \right) \geq 0 \end{aligned} \tag{3.6}$$

  So reaching thermodynamic equilibrium by reaching the same temperature everywhere in the system is always a spontaneous, i.e. irreversible process since only for $T_1 = T_2$ we get $\Delta S = 0$.

- Calculate ΔS when one mol of a perfect gas is irreversibly expanded in an adiabatic process: 300 K, 1 bar → 240 K, 0.5 bar. As a reversible change in state we can choose
  - Rev. isothermal expansion: 300 K, 1 bar → 300 K, 0.5 bar, $\Delta S_1 > 0$
  - Rev. isobaric cooling: 300 K, 0.5 bar → 240 K, 0.5 bar, $\Delta S_2 < 0$

  $\Delta S_{tot} = \Delta S_1 + \Delta S_2 > 0$ (!), despite the fact that the complete process is adiabatic. ΔS_{tot} represents the excess entropy based on the irreversibility of the process.