

3.2 Entropy

The entropy is defined via its variation as (the absolute value of S will be discussed later):

$$\begin{aligned} dS &= \delta q_{rev}/T && \text{for reversible process} \\ dS &> \delta q_{rev}/T && \text{for irreversible process} \end{aligned} \quad (3.1)$$

So for the same heat transfer a larger increase of entropy is found when heating a cold compared to a warm bath. BUT we have a larger entropy in the warm bath.

Why is it impossible for an isolated system to find $\Delta S_{total} < 0$? We will discuss a system with warm subsystem 1 at T_1 and cold subsystem 2 at T_2 . So heat δq will flow from subsystem 1 into subsystem 2, i.e.

$$\Delta S_{total} = \frac{\delta q}{T_2} - \frac{\delta q}{T_1} > 0 \quad \text{since } T_1 > T_2 \quad (3.2)$$

The opposite sign $\Delta S_{total} < 0$ would be against all experience: no heat will flow spontaneously from cold to hot!

- The general problem about entropy deals with the fact that we need the equal sign ("=") in Eq. (3.1) to do calculations. But since S is a state function one can find always an alternative reversible path for describing irreversible changes.
- The first law is of course applied to express δq by expansion work and C_v , respectively.