# CHAPTER 4 - Reversibility and the Second Law

When we presented Postulate III, we implied that not all processes between two states of a closed system are "adiabatically accessible". In this lecture, we will clarify which processes are feasible, and introduce the concept of entropy.

Consider two possible states of a closed, adiabatic system:

| STATE A | STATE B |
| --- | --- |
| (1) Two immiscible fluids at therm. temp. $\theta_1$ and $\theta_2$ | The two fluids at the same $\theta$. |
| (2) A fermentation tank in which cells are growing happily | Dead cells and debris floating around |

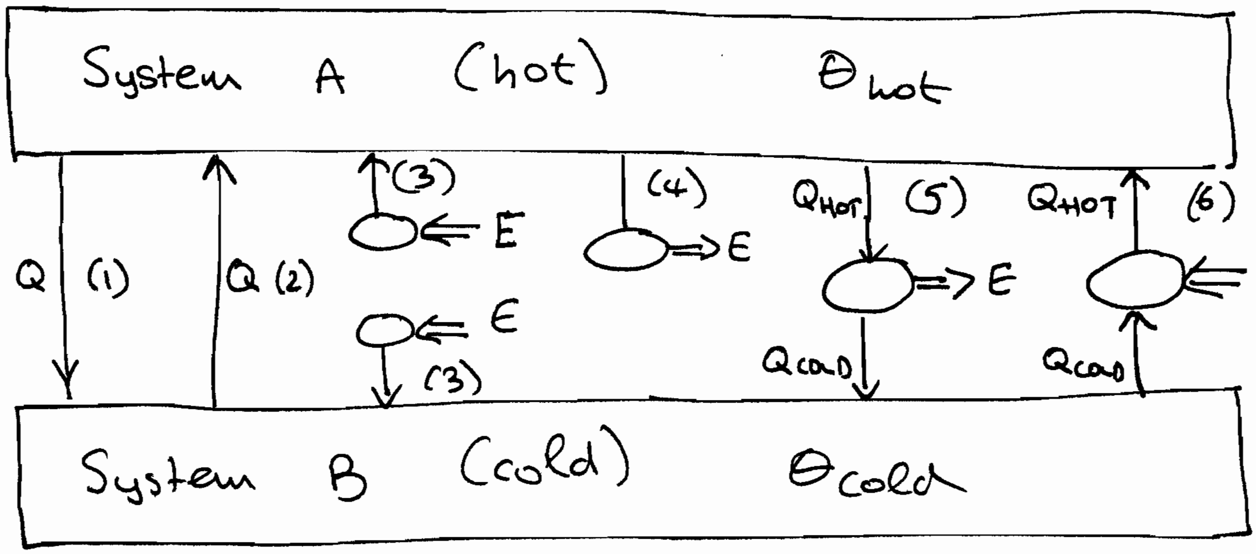
In both cases, the first Law suggests that

$$\underline{E}_A = \underline{E}_B$$

Experience dictates that if we have a system in state A, leave it alone and come back in a few weeks, we will observe state B, while the opposite is never observed.

Postulate II states that any system will evolve towards a stable equilibrium state, but does not give a prescription for predicting what it will be. To investigate this question, we need to consider simple devices that undergo heat interactions with one or more systems, and work interactions with an energy reservoir. These "heat engines" can be any mechanism (e.g. living cells!)

Convention: We use a scale of thermometric temperatures so that $\underline{E} \uparrow$ as $\theta \uparrow$ – the opposite choice is also valid, and is used in Stat. mech.




Are any of these processes disallowed by the Postulates?

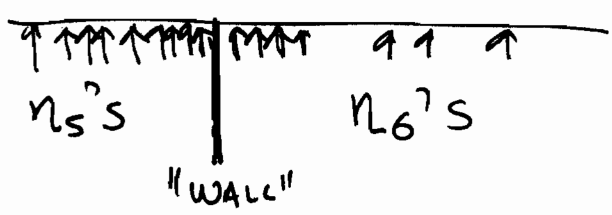
① OK
② Violates Post.-II
③ OK
④ In combination with (3) = 2 → not allowed
(5), (6) } OK, But there must be restrictions on magnitude of E, otherwise a combination of (5) and (6) is (2).

Define "efficiency": $\eta_5 = -\dfrac{E}{Q_{HOT}}$ $[E- \; Q+]$ $\qquad \eta_6 = -\dfrac{E}{Q_{HOT}}$ $[E+ \; Q-]$

Must have: $\eta_5 \leq \eta_6$ $\qquad \eta_6$ can be $>1$!

↳ Can $\eta_5$ be $<0$? yes!

For a given pair of $\theta_{HOT}$, $\theta_{COLD}$,




All $\eta_5$'s must be less than any $\eta_6$, and the reverse.

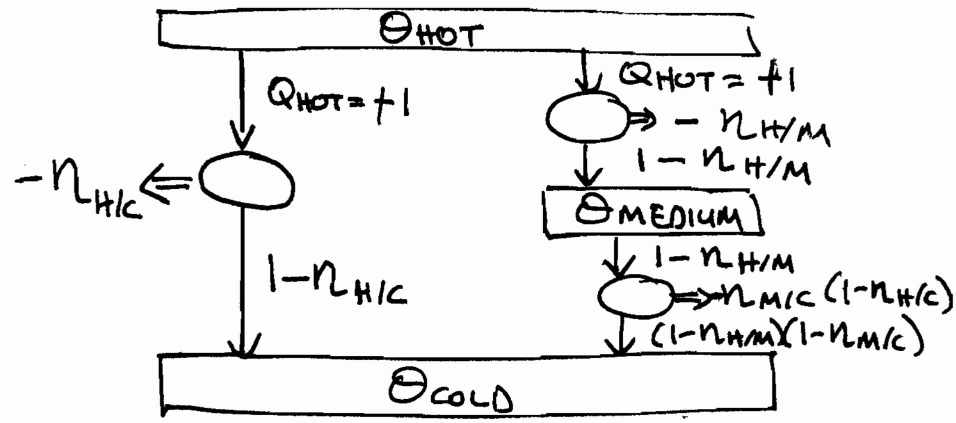
The "wall" separating all $\eta_S$'s from $\eta_G$'s represents a limit:

When a second process could be performed in at least one way so that the system and all elements of the environment are restored to their initial states, the process is called <u>reversible</u>.

For reversible processes (and only for rev. proc.)

$$\boxed{\eta_S^{rev} = \eta_G^{rev} = \eta_{rev}}$$

For reversible processes:




Must have: $(1-\eta_{H/M})(1-\eta_{M/C}) = (1-\eta_{H/C})$

for <u>any</u> $\Theta_{medium}$

This can only happen if $1-\eta_{A/B} = \dfrac{f(\Theta_A)}{f(\Theta_B)}$

Since $(1-\eta_{A/B})$ is universal (does not depend on the system used), $f(\Theta_A)$ is also a universal function, within a multiplicative constant.

We <u>define</u> the thermodynamic temperature using $f(\Theta)$. Is $f(\Theta) = T$ a good choice?

$$f(\Theta) = T \Rightarrow 1-\eta_{H/C} = \frac{T_H}{T_C} \Rightarrow \eta = \frac{T_C - T_H}{T_C} \lt 0 \Rightarrow$$

$\Rightarrow T_C > T_H$ × not consistent with $\theta_H > \theta_C$

$f(\theta) = 1/T$ $\qquad 1 - \eta_{H/C} = \frac{T_C}{T_H} \Rightarrow \boxed{\eta = \frac{T_H - T_C}{T_H}}$ ✓

Almost by coincidence the temperature scale defined by $T_{\text{ideal gas}} \underset{\lim P\to 0}{\equiv} \frac{P\underline{V}}{nR}$ and $\frac{T_C}{T_H} = 1 - \eta$ are identical.

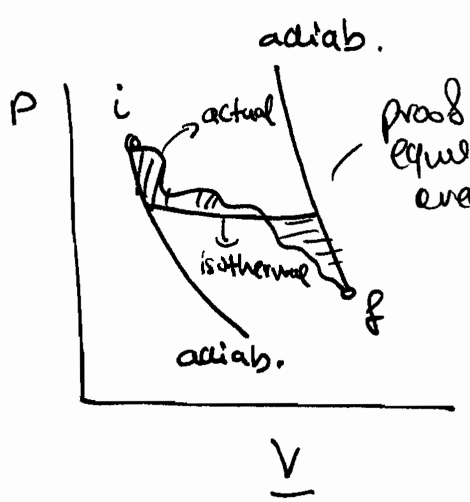
<u>Theorem of Clausius</u>

$\downarrow Q_H$

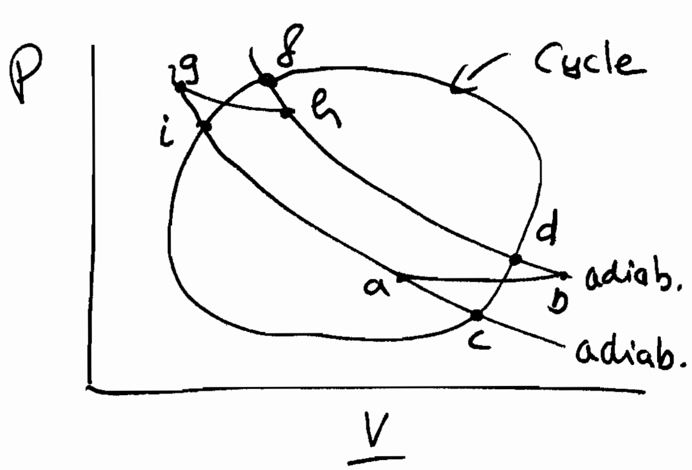
$\Rightarrow \epsilon = \eta Q_H$

$\downarrow Q_C = -(1-\eta) Q_H = -\frac{T_C}{T_H} Q_H \Rightarrow \boxed{\frac{Q_C}{T_C} + \frac{Q_H}{T_H} = 0}$

for reversible process




For any reversible process one can find a reversible process consisting of adiabatic-isothermal-adiabatic steps such that the heat interaction in the isothermal step is equal to the heat interaction in the actual process




path $ighdba$ is equivalent to $ifdc$

$$\frac{Q_{if}}{T_{if}} + \frac{Q_{cD}}{T_{cD}} = 0$$

At the limit of short steps if and cd

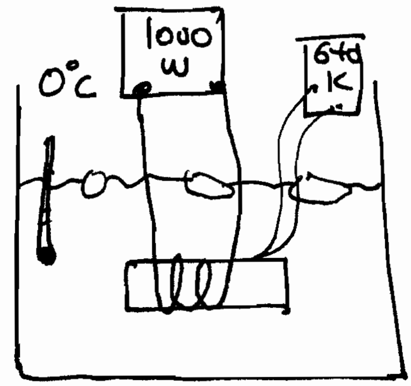
$$\frac{\delta Q_{if}}{T_{if}} + \frac{\delta Q_{cd}}{T_{cd}} \Rightarrow \oint \left(\frac{\delta Q}{T}\right)_{rev} = \phi$$

This allows us to define a new state function, the entropy $\underline{S}$ :

$$\Delta \underline{S} = \int_A^B \left(\frac{\delta Q}{T}\right)_{rev} \qquad d\underline{S} = \left(\frac{\delta Q}{T}\right)_{rev}$$

How do we calculate entropy changes?

<u>Example 4.2</u>




Bar of aluminum in ice bath
Current is passed at 1000 W
"Film boiling is occuring at the interface with noisy collapse of the bubbles."

What is the entropy change of the bar, water and the universe per s of operation?

<u>Ans</u>: Ignore <u>actual</u> process, imagine a reversible process for each part of the system:

Ice: $\Delta \underline{S}_{ice} = \frac{Q}{T} = + \frac{1000}{273} \frac{J}{K}$ Bar: $\Delta \underline{S} = \phi$ (no change!)

Universe: $\Delta \underline{S} = \Delta \underline{S}_{ICE} = + \frac{1000}{273} \frac{J}{K}$