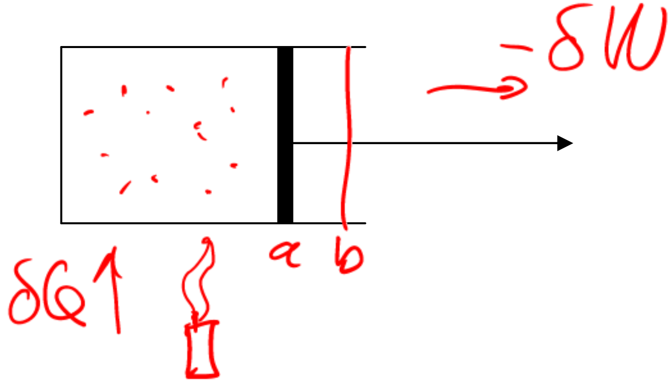
Chapter 1.4: Thermodynamic processes

Goal: generate work from heat



Example: isothermal expansion

$T = \text{const.}$

$E = \text{const.}$

$\delta Q + \delta W = 0$

Ideal gas laws: $E = \frac{3}{2} N k_B T$ $\qquad pV = N k_B T$

classical monoatomic gas

k_B = Boltzmann konstant

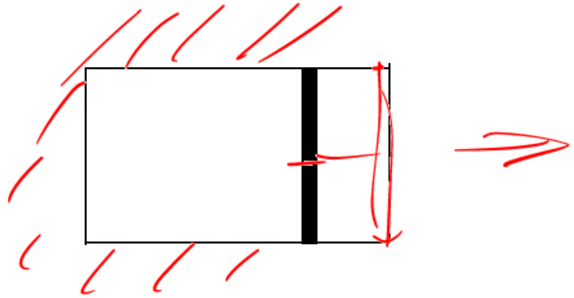
$$\Delta W = -\int_a^b p\,dV = -\int_a^b \frac{N k_B T}{V}\,dV = N k_B T \ln \frac{V_a}{V_b} = -\Delta Q < 0$$

$V_b \to \infty$: $-\delta W \to \infty$ not practical because of ln.

1.4-2 Thermodynamic processes

We know $\Delta E = \Delta Q + \Delta W$ but $\Delta Q, \Delta W$ are not unique

Guy Lussac thought experiment (1807)



Reversible and irreversible expansion

d

$\Delta W = 0$

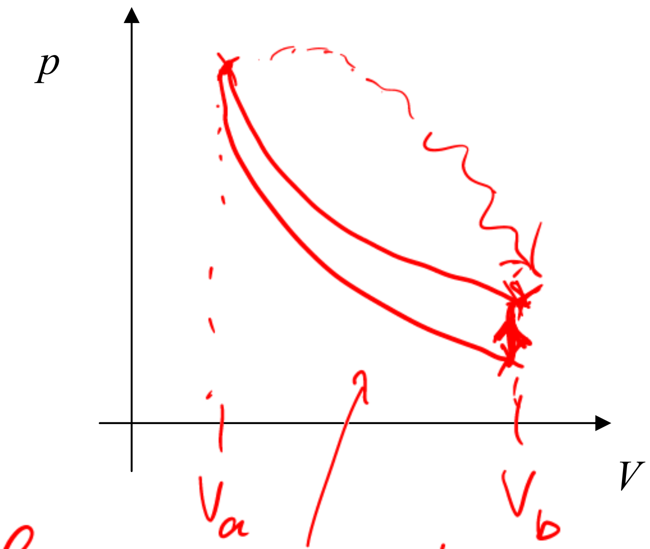
$p = \frac{N k_B T}{V}$

adiabatic expansion

$\Delta Q = 0$

$\Delta W \neq 0$ see exercise 3

$-\Delta W_{adiabatic} < -\Delta W_{isothermal}$



$-\Delta W = \int_a^b p\,dV$

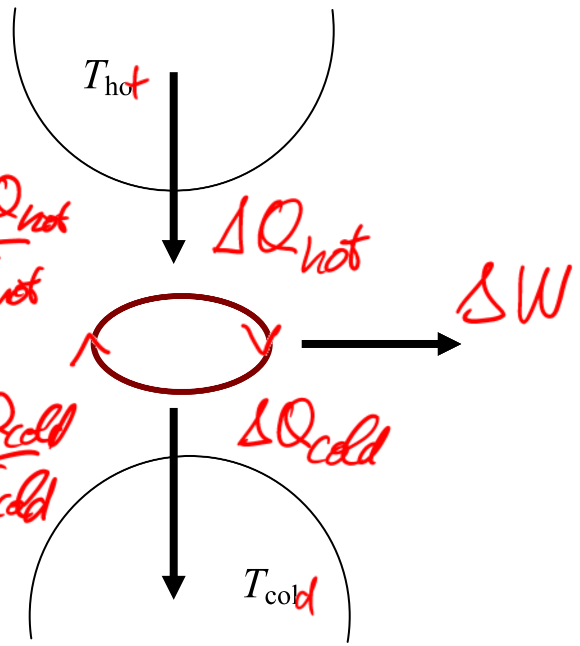
Def. 1.12: A reversible cyclic process periodically takes a work-substance through a cycle of equilibrium states under exchange of heat and work only.

Practically: Stirling engine, heat pumps, refrigerator

Work substance does not get exchanged

but δQ, δW

$$\Delta E = \Delta Q + \Delta W = 0$$



$$\Delta S_{hot} = \frac{\Delta Q_{hot}}{T_{hot}}$$

$$\Delta S_{cold} = \frac{\Delta Q_{cold}}{T_{cold}}$$

$\Delta W < 0$ for engines

but $\Delta W > 0$ for refrigerator or heat pump

$$\Delta W + \Delta Q_{hot} + \Delta Q_{cold} = \Delta E = 0$$

true for reversible and irreversible cycles

$\Delta S_{hot} + \Delta S_{cold} = 0$ for reversible cycles

$$\Rightarrow \frac{\Delta Q_{hot}}{T_{hot}} = - \frac{\delta Q_{cold}}{T_{cold}}$$

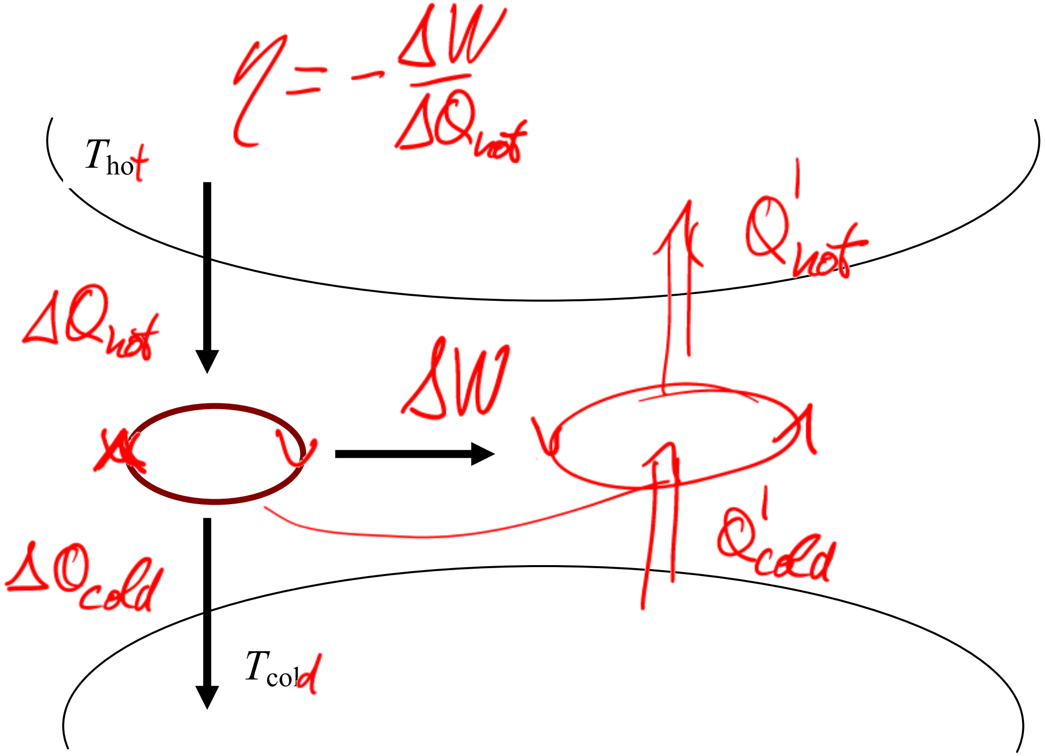
$$\Delta S_{hot} + \delta S_{cold} > 0$$

Def. 1.13: The efficiency of a reversible cyclic process as an engine is $\eta = -\frac{\Delta W}{\Delta Q_{\mathrm{hot}}} = \frac{\Delta Q_{hot} + \Delta Q_{cold}}{\Delta Q_{hot}}$

$$= 1 + \frac{\Delta Q_{cold}}{\Delta Q_{hot}} < 1$$

$$= 1 - \frac{T_{cold}}{T_{hot}}$$

All reversible cyclic processes have the same efficiency as a function of T_{hot} and T_{cold}



$$\eta' = -\frac{\Delta W}{\Delta Q'_{hot}}$$

assume $\eta' < \eta$

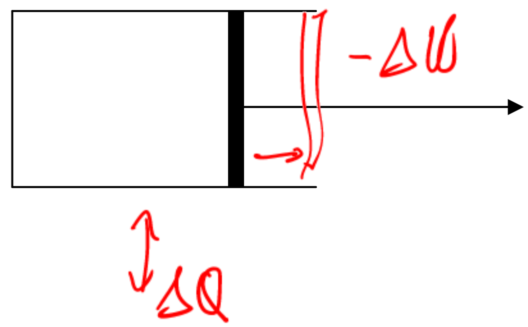
$\Delta Q'_{hot} > \Delta Q_{hot}$

Clausius 1850

not spontaneous ΔQ from T_{cold} to T_{hot}

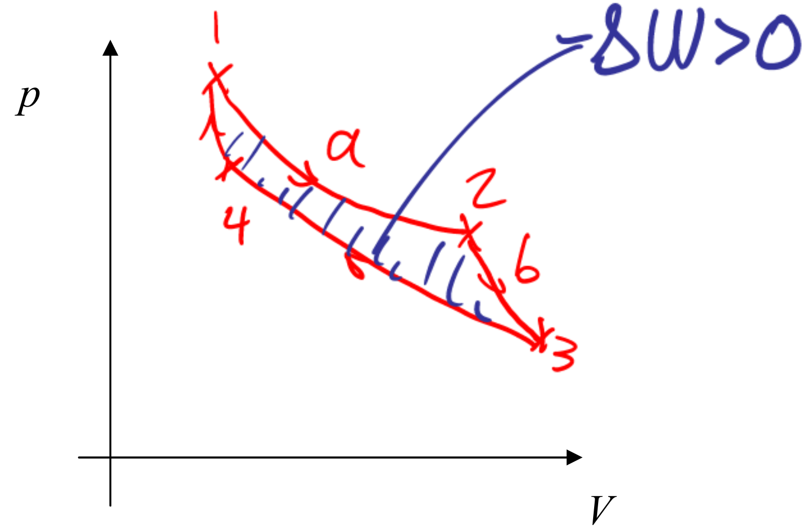
$\Longrightarrow \eta = \eta'$

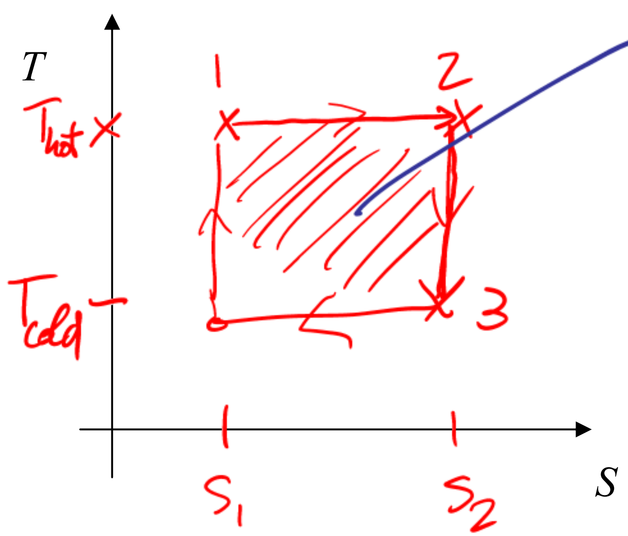
Carnot cycle



$pV = N k_B T$

$E = \frac{3}{2} N k_B T$





$\delta Q_{hot} + \delta Q_{cold} = -\delta W = (T_{hot} - T_{cold})(S_2 - S_1)$

a) isothermal expansion

$\delta W = N k_B T_{hot} \ln \frac{V_1}{V_2} < 0 \qquad \delta Q_{hot} = \int_1^2 T\,dS = T_{hot}(S_2 - S_1) > 0$

b) $\Delta Q = 0$; $\delta S = 0$

adiabatic expansion $\delta W < 0$

c) isothermal compression

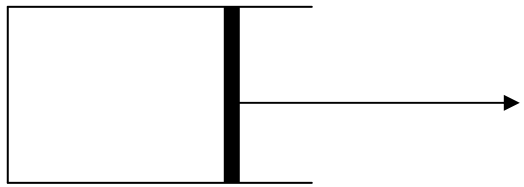
$\delta Q_{cold} = T_{cold}(S_1 - S_2) < 0$

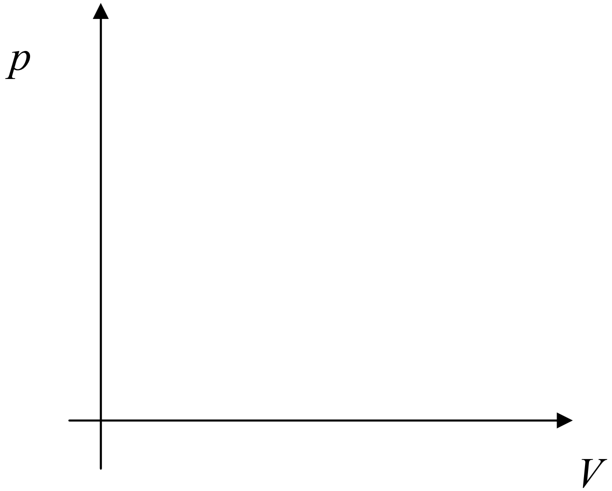
d) adiabatic compression

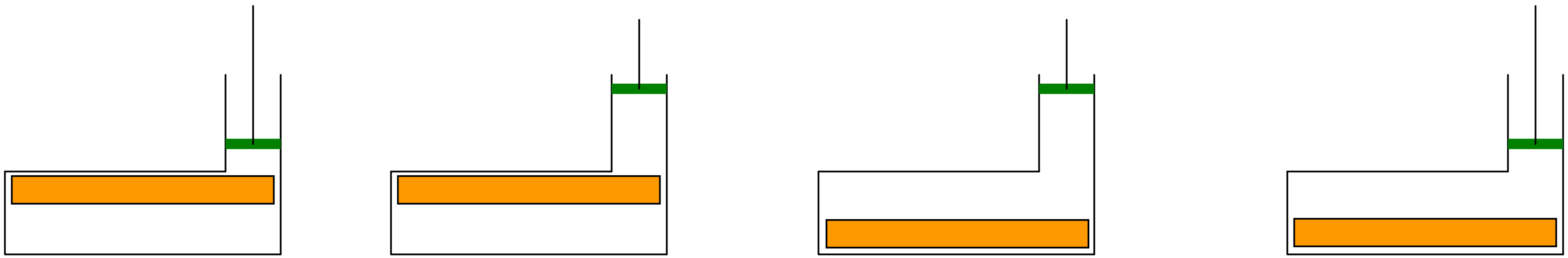
$$\eta_{Carnot} = -\frac{\Delta W}{\Delta Q_{hot}} = \frac{(T_{hot} - T_{cold})(S_2 - S_1)}{T_{hot}(S_2 - S_1)} = 1 - \frac{T_{cold}}{T_{hot}}$$

The efficiency of all reversible cyclic processes is $\eta = -\frac{\Delta W}{\Delta Q_{\mathrm{hot}}} = 1 - \frac{T_{\mathrm{hot}}}{T_{\mathrm{cold}}}$

Stirling cycle





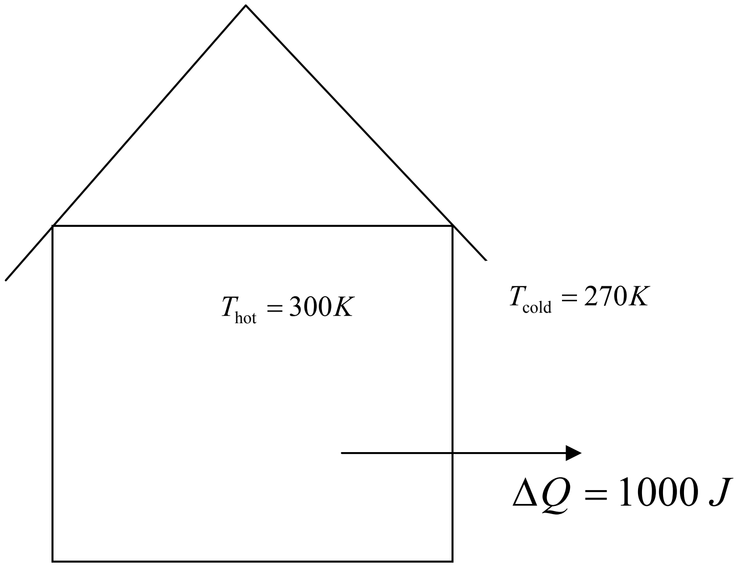


Non reversible engines: real machines

Coal powered plants:

Theoretical: $T_{\text{hot}} = 2100\,K$ $T_{\text{cold}} = 300\,K$ $\eta = -\dfrac{\Delta W}{\Delta Q_{\text{hot}}} = 1 - \dfrac{T_{\text{hot}}}{T_{\text{hot}}} = 0.85$

Examples: heating and cooling



$$\Delta S = \Delta Q\left(\frac{1}{T_{cold}} - \frac{1}{T_{hot}}\right) \approx 0.37\,\frac{J}{K}$$