Entropy cont/d

Review:

Entropy change $\Delta S = \int \frac{dQ}{T}$ between states

For ideal gas: $dQ = dE_{int} + dW$
$= nc_v dT + p dV$

$\Rightarrow \Delta S = nc_v \ln\left(\frac{T_f}{T_i}\right) + nR\ln\left(\frac{V_f}{V_i}\right)$

OR $\Delta S = nc_v \ln\left(\frac{P_f}{P_i}\right) + n\underbrace{(c_v+R)}_{c_p}\ln\left(\frac{V_f}{V_i}\right)$

$= 0$ for adiabatic processes

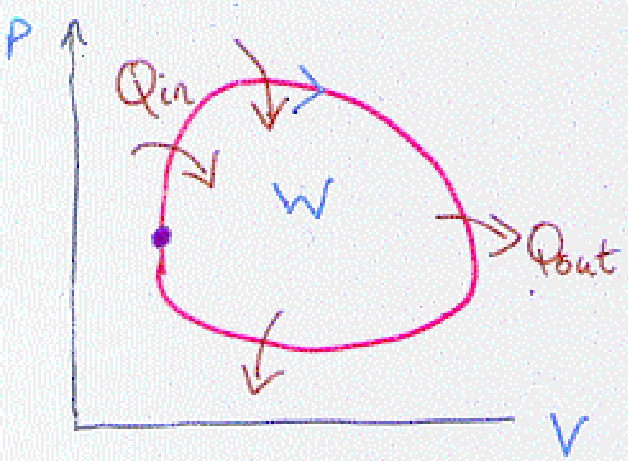
(defines contours of constant S on P-V diagram)

Engines:

Extract heat, transform some heat → work (piston $\int PdV$)

* operate in a cycle: working substance* returns to original state with $\Delta E_{int} = 0$, $\Delta S = 0$

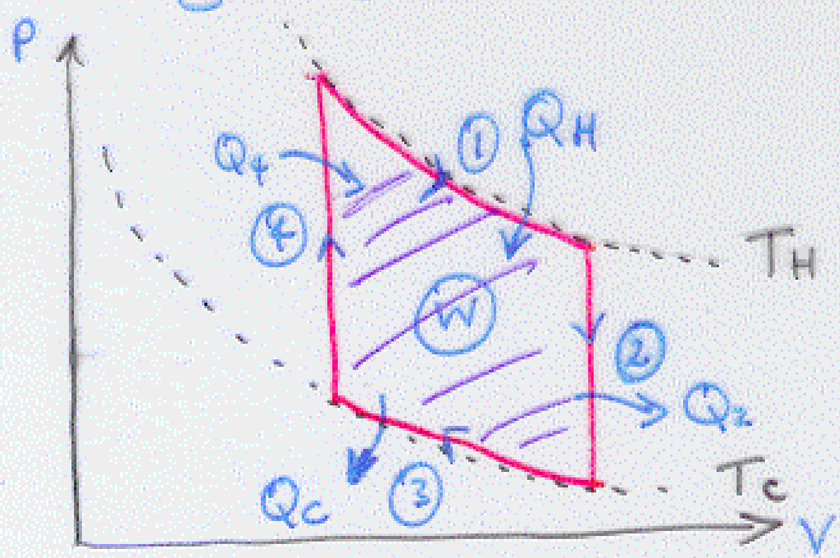
$\therefore \Delta Q = Q_{in} - Q_{out}$
$= \text{Work } W$



e.g. air/fuel mix (replaced)

steam ⇄ water (recycled)

e.g. Stirling Engine



1. Isothermal expansion does work, absorbs Q_H
2. Isochoric cooling $T_H \to T_C$, ejects Q_2
3. Isothermal compression at T_C, ejects Q_C, work required
4. Isochoric heating $T_C \to T_H$, absorbs Q_4

For this engine, $Q_4 = -Q_2 = \Delta E_{int} = nc_V(T_H - T_C)$

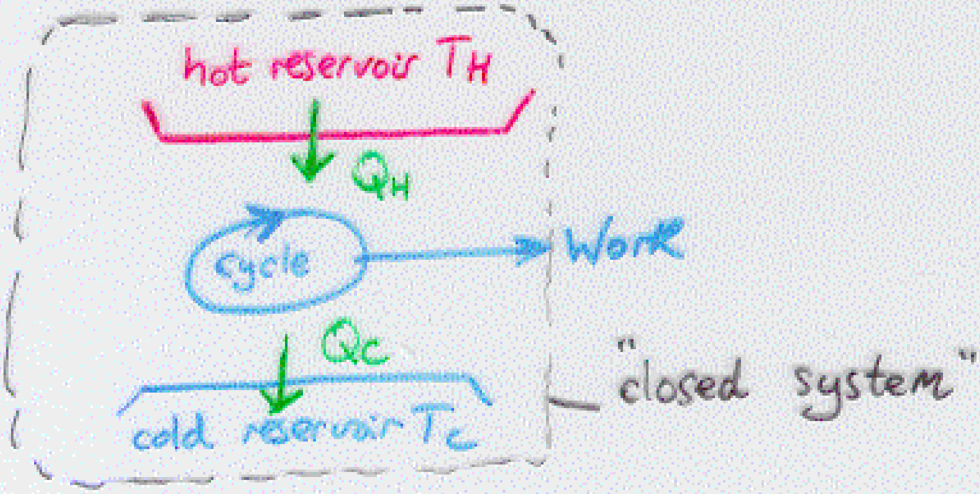
$\Rightarrow$ net heat input $= Q_H - Q_C$

$= \text{work done by gas } W$

Note: Clockwise cycle always does positive work

Practise: For any path on P-V diagram, is $Q = nc_V \Delta T + \int P\,dV$
>0
<0
$=0$ adiabatic ?

"Ideal" Engine Cycle (e.g. Carnot cycle)



- Closed cycle with $\Delta E_{int} = 0$ for working substance (e.g. exhaust air at outside temp)
- Net heat transfer between reservoirs only (all other transfers <u>reversible</u> $\Rightarrow$ no friction $\Rightarrow$ engine stays cool!)

$\Rightarrow$ Work $W = Q_H - Q_C$ (1st law) and

for system $\Delta S = 0$ (reversible cycle)

Working substance : $\Delta S_W = 0$ (returns to same state)

Hot res : $\Delta S_H = -Q_H / T_H$

Cold res : $\Delta S_C = Q_C / T_C$

So $\Delta S = 0 \Rightarrow \left|\frac{Q_H}{T_H}\right| = \left|\frac{Q_C}{T_C}\right|$ (ideal engine)

Efficiency of Ideal Engine

Previously: $W = Q_H - Q_c$ and $\frac{|Q_H|}{T_H} = \frac{|Q_c|}{T_c}$ (ideal) (*)

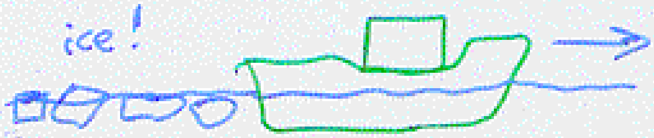
Define: Efficiency $\varepsilon = \frac{W}{Q_H} = \frac{\text{work done}}{\text{heat input}} = 1 - \frac{|Q_c|}{|Q_H|}$

$$\boxed{\text{For ideal engine, } \varepsilon = 1 - T_c/T_H \text{ due to } (*)}$$

Consequences:

- No engine 100% efficient! ("Perfect" engine would transform all of Q_H into work: only possible if $T_c = 0$ or $T_H \to \infty$)

Otherwise:



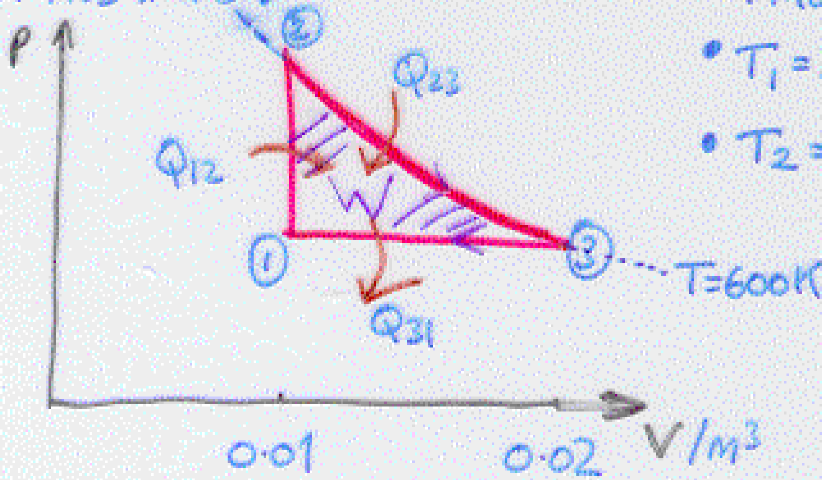
Boat extracts heat from water (so water → ice), then converts heat to work ✗

2nd law: heat will not flow from water → boiler room
(c.f. ball rolling uphill!)

Also note: Work done ($\varepsilon > 0$) only when heat flows $T_H \to T_c$; must have a colder place to dump heat (otherwise – "heat death" when T same everywhere)

Non-Ideal Engine Cycle - Example

Ch21 Prob #43:



- 1 mole of gas (monatomic)
- $T_1 = 300K$, $V_1 = 0.01 m^3$
- $T_2 = T_3 = 600K$

$\Rightarrow V_3 = 0.02 m^3$

a) Heat absorbed in cycle Q_H ?

$$Q_{12} = \Delta E_{int} = \tfrac{3}{2} n C_v \Delta T = \tfrac{3}{2} R (600K - 300K) = 3.74 kJ$$

$$Q_{23} = \underbrace{\Delta E_{int}}_{=0} + \int P.dV = nRT \ln\left(\frac{V_3}{V_2}\right) = nR(600K)\ln 2 = 3.46 kJ$$

$\Rightarrow$ Heat input $Q_H = 3.74 + 3.46 = 7.20 kJ$

b) Heat output $Q_C = Q_{31} = n C_p \Delta T = \tfrac{5}{2} R (300-600) = (-) 6.23 kJ$

c) Work done $W = \underbrace{Q_{12} + Q_{23}}_{Q_H} + \underbrace{Q_{31}}_{Q_C}$, since $\Delta E_{int} = 0$ around cycle

i.e. $W = 7.20 - 6.23 = 0.97 kJ$

d) $\therefore$ Efficiency $\varepsilon = \dfrac{W}{Q_H} = \dfrac{0.97 kJ}{7.20 kJ} = 14\%$

c.f. Ideal engine cycle operating between T_H, T_C

$$\varepsilon_{ideal} = 1 - \frac{T_C}{T_H} = 1 - \frac{300K}{600K} = 0.5 \text{ or } 50\%$$