Microscopic Entropy.

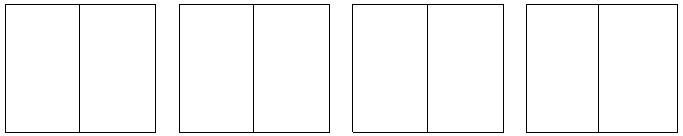
Microscopic def. -

- measure of the molecular disorder of the system. Its value is related to the number of microscopic states available at a particular macroscopic state.
  - $\underline{S}_i = k \ln (p_i)$ or $\Delta \underline{S} = k \ln (p_2/p_1)$

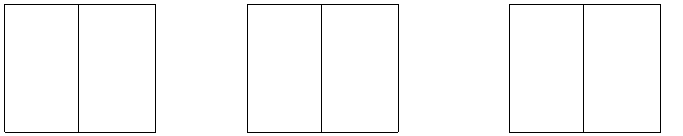
  where p_i is the number of *distinguishable* microstates in the *i*th macrostate.
- # microstates - number of equivalent ways of macroscopic arrangement.
- macrostate - distinct arrangement of molecules.

Configurational Entropy

Microstates

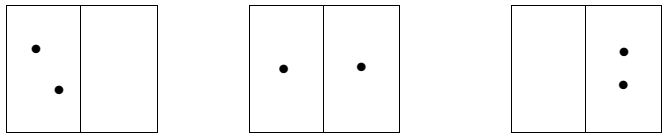


Macrostates



$\underline{S}_i = k\ln(1)$ $\underline{S}_i = k\ln(2)$ $\underline{S}_i = k\ln(1)$

Macrostates



$$\underline{S} = k\ln\frac{N!}{\prod_{i=1}^{M} m_i!}$$

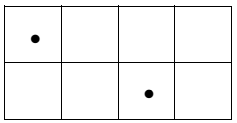
N particles, M boxes, m_i in box i

! - factorial, $5! = 5 \cdot 4 \cdot 3 \cdot 2 \cdot 1$

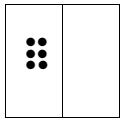
Note 0!=1

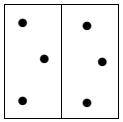
$\underline{S}_i = k\ln\frac{2!}{1!1!} = k\ln(2)$ $\underline{S}_i = k\ln\frac{2!}{0!2!} = k\ln(1)$

Can divide space into equal sized boxes

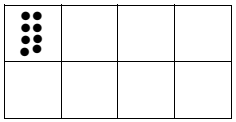


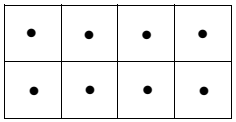
Expand Volume





$$\underline{S}_i = k\ln\frac{6!}{6!0!} = k\ln(1)$$





$$\underline{S}_i = k\ln\frac{8!}{8!0!\ldots0!}$$

$$= k\ln(1)$$

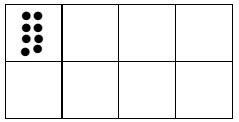
Stirling's Approximation

For N > 100

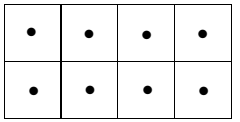
$$\ln N! \approx N\ln N - N$$

$$k\ln N! \approx Nk\ln N - N \approx nR\ln N - N$$

Let each dot represent 1000 molecules



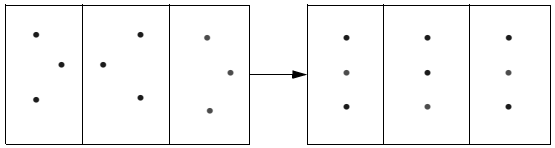
$$\underline{S}_i = k\ln\frac{N!}{N!0!\ldots0!}$$



$$\underline{S}_i = k\ln\frac{N!}{\left(\frac{N}{8}\right)!\left(\frac{N}{8}\right)!\ldots\left(\frac{N}{8}\right)!}$$

Entropy change of mixing

Let each dot represent 1000 particles,



blue $\Delta\underline{S}_{blue} = n_{blue}R\ln\frac{3}{2}$

red $\Delta\underline{S}_{red} = n_{red}R\ln\frac{3}{1}$

$$\frac{3}{1}N_{red} = \frac{3}{2}N_{blue} = N_{total}$$

Entropy of mixing

3.3 MACROSCOPIC DEFINITION OF ENTROPY

- THE SECOND LAW OF THERMODYNAMICS states that reversible processes and/or optimum work interactions occur *without entropy generation*.
- Irreversible - increase in entropy of universe, (lost work).
- Reversible - no increase in entropy of the universe. (no entropy generation).
- Proposed processes that would result in a decrease in the entropy of the universe are impossible.

ENTROPY DEFINITION (Macroscopic)

$$dS \equiv \frac{dQ_{rev}}{T_{sys}}$$

$$\Delta S = \int \frac{dQ_{rev}}{T_{sys}}$$

a. any rev. path

b. T_{sys} is system property

Calculating S

$$d[U + KE + PE] = dQ + dW_S - PdV$$

Constant pressure path

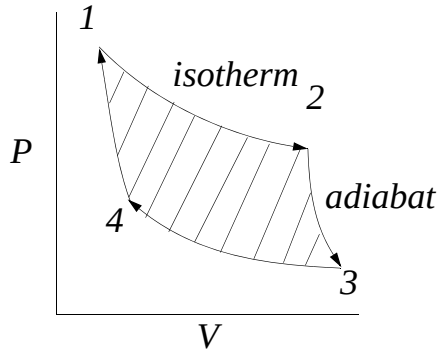
Constant volume path

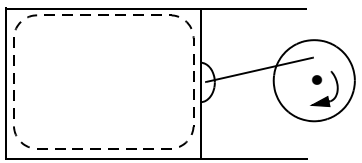
$$\Delta S = \int \frac{dU}{T_{sys}} = \qquad \Delta S = C_V \ln \frac{T_2}{T_1} \quad (*)$$

Isothermal path (*ig)*

$$dQ = dU + PdV =$$

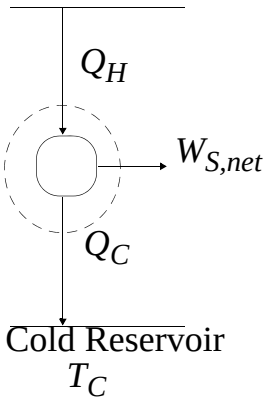
3.5 Carnot Engine, Thermal Efficiency





Thermal Efficiency (Greatest for Carnot Engine)

$$\eta \equiv \frac{\text{net work ouput}}{\text{heat input}} = \frac{-\dot{W}_{S,\,net}}{\dot{Q}_H}$$



Energy Balance

$$-\dot{W}_{s,\,net} = \dot{Q}_H + \dot{Q}_C$$

Definition

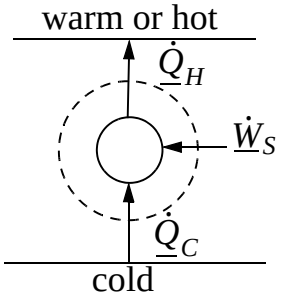
$$\eta \equiv -\frac{\dot{W}_{S,\,net}}{\dot{Q}_H} = 1 + \frac{\dot{Q}_C}{\dot{Q}_H}$$

Entropy Balance for boundary

$$\Delta \dot{S} = 0 = \frac{\dot{Q}^{in}}{T_H} + \frac{\dot{Q}^{out}}{T_C} = \frac{\dot{Q}_H}{T_H} + \frac{\dot{Q}_C}{T_C}$$

$$\frac{\dot{Q}_C}{\dot{Q}_H} = -\frac{T_C}{T_H} \qquad \eta = 1 - \frac{T_C}{T_H}$$

3.6 Carnot Heat Pump



E-bal

S-bal

$$0 = \dot{S} = \frac{\dot{Q}_H}{T_H} + \frac{\dot{Q}_C}{T_C}$$

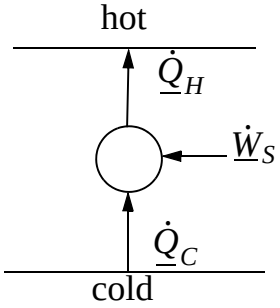
$$\dot{Q}_H = -\left(\frac{T_H}{T_C}\right)\dot{Q}_C$$

•Coefficient of Performance

$$COP \equiv \frac{\dot{Q}_C}{\dot{W}_S} =$$

3.7 Internal Reversibility

•Maximum efficiency (or COP) when Carnot temperatures match reservoir temperatures.



3.8 Real Process Equipment

- Outlet pressure will match reversible device.
- Outlet enthalpy will be higher.
- efficiency:

- pump, compressor $\eta = \frac{\underline{W}_{rev}}{\underline{W}_{act}} \cdot 100\%$

- turbine, expander $\eta = \frac{\underline{W}_{act}}{\underline{W}_{rev}} \cdot 100\%$

Process Schematics

turbine

compressor

pump

heat exchanger

3.9 Entropy Balances

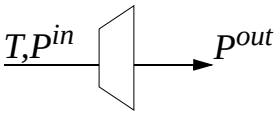
Adiabatic Turbine, Compressor, Pump

$$\frac{d\underline{S}}{dt} = \sum_{in} S^{in}\dot{m}^{in} - \sum_{out} S^{out}\dot{m}^{out} + \frac{\dot{Q}}{T_{sys}} + \underline{\dot{S}}_{gen}$$

Turbine Calculations:

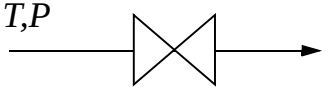
- $\eta = \frac{\Delta\underline{H}}{\Delta\underline{H}'} \cdot 100\%$ where

$\Delta\underline{H}'$ is reversible($\Delta S' = 0$)



Valve

Steady-State T,P



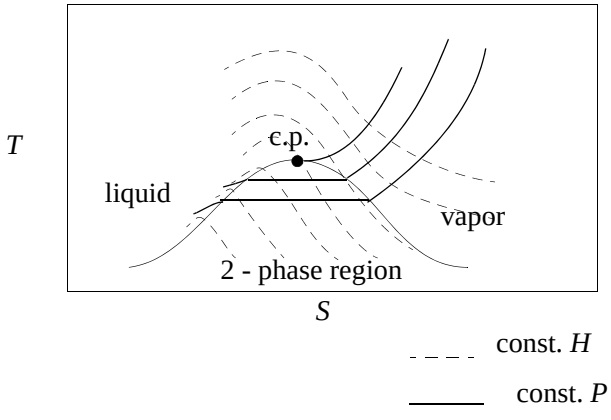
By Energy Balance

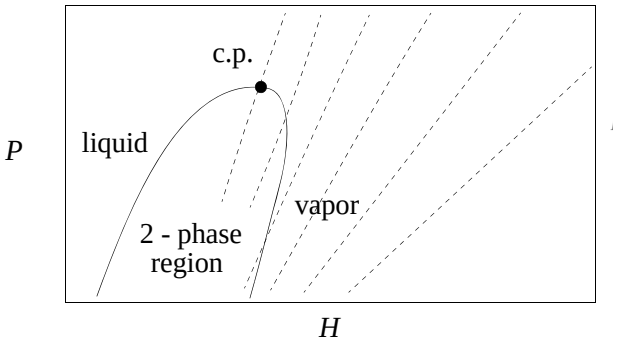
valves irreversible

for ig $\Delta S = C_p \ln\left(\frac{T^{out}}{T^{in}}\right) - R\ln\frac{P^{out}}{P^{in}}$ (*ig)

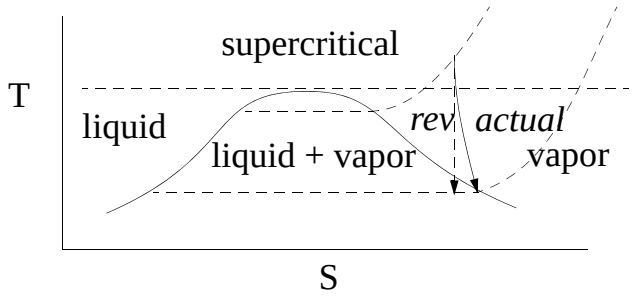
Nozzles (gas flow)

3.10 Charts including Entropy

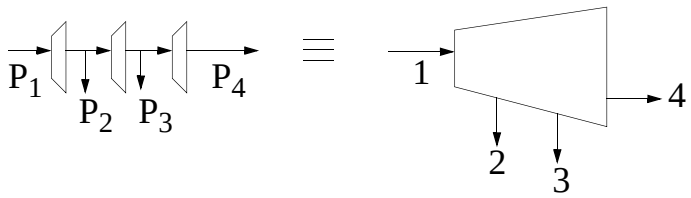


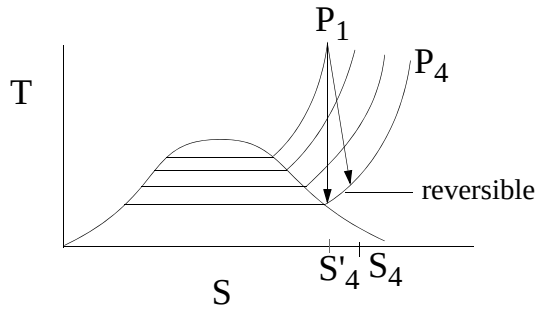


3.11 Steam Turbine Calculations



3.12 Multistage Turbines

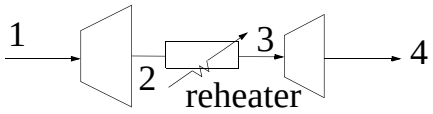




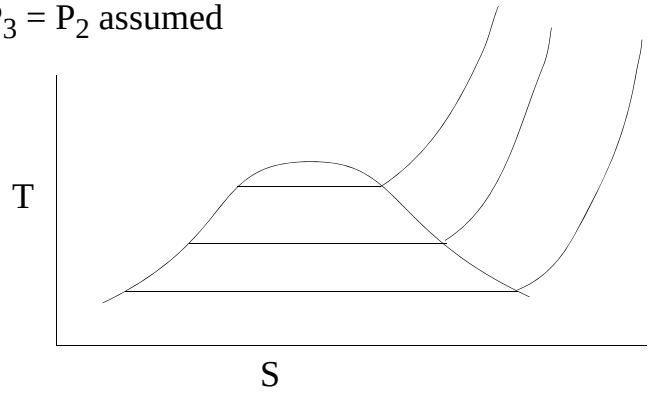
only the last stage near saturation if no reheat

$H_2 = H_1 + \eta\Delta H'$

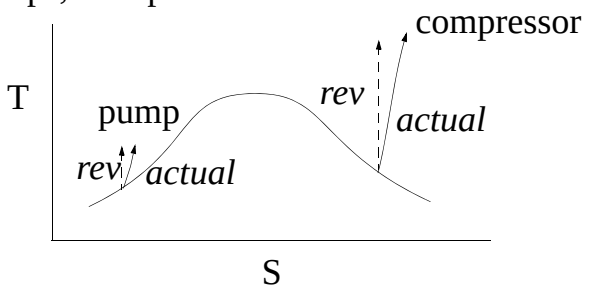
Multistage turbines with Reheat

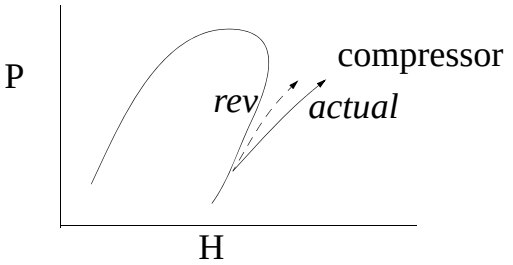


$P_3 = P_2$ assumed

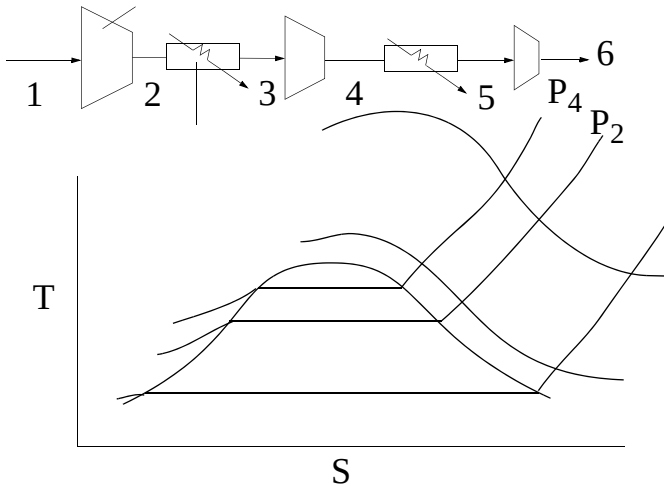


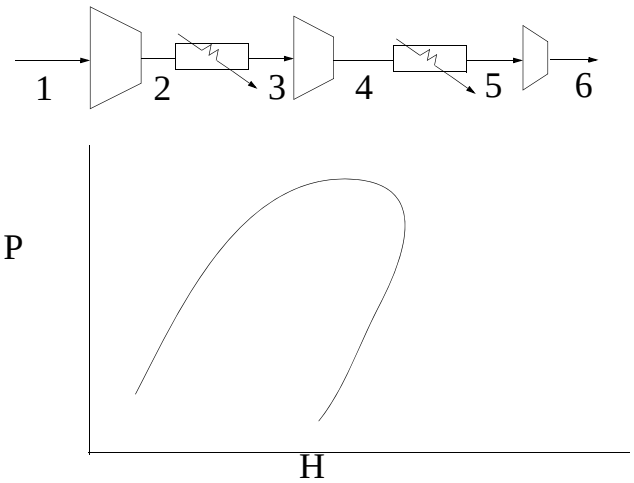
3.13 Pumps, Compressors





3.13 Multistage Compression





Strategies for applying the S-balance.

New terms -

Is S-balance needed?

S_{gen} usually not pointed out.