

EGR3030 – Energy Systems and Conversion

Week 2 lecture - Gas laws and entropy

The concept of entropy, deriving its relationships for closed open (flow) systems Application of entropy to quantify the loss of efficiency of systems (such as turbines and compressors) due to irreversibilities.

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Learning outcomes

- Gas laws revision
- Entropy
- Entropy property diagrams (for Carnot Cycle)
- Evaluation of entropy for common substances
- Evaluation of entropy for isothermal/non-isothermal processes
- Isentropic processes
 - For pumps/compressors
 - Turbines
 - Nozzles

Intro video: quick refresher to the gas laws



<https://youtu.be/pUhZWQkkTqY>

The ideal gas law (summary)

- $PV = k_1$ (Boyle's law, 1662, $P \propto 1/V$) – assumption:
constant temperature
- $V/T = k_2$ (Charles' law, 1787, $V \propto T_{abs}$) – assumption:
constant pressure
- $P/T = k_3$ (Gay-Lussac's law, 1809, $P \propto T$) – assumption:
constant volume

When combined, $\frac{PV}{T} = k_1 \cdot k_2$ or $\frac{PV}{T} = k_3$

This can also be written as $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

- $V/n = k_4$ (Avogadro's law, 1812, $V \propto n$) where n is the number of molecules – assumption:
constant P, T
- Combining $PV/T = k_3$ with $V/n = k_4$ gives:

$$\frac{PV}{nT} = k_5$$

$$\frac{PV}{nT} = R$$

where R is the universal gas constant =
8.31447 kJ/(kmol.K)

The gas constant (not universal) is gas
specific: $R_{gas} = \frac{R_U}{M_M}$.

Where R_U is the universal gas constant
and M_M is molecular mass of gas
concerned.

Class exercise

- What is the mass and density of 22.7 litres of H_2 @ STP?

Table A-1 molar mass $H_2 = 2.016g$

$$2.016/22.7 = 0.0888 \text{ g/litre}$$

- What is the mass and density of 22.7 litres of Air @ STP?

Table A-1 molar mass Air = 28.97g

$$28.97/22.7 = 1.2762g/litre$$

Entropy



https://youtu.be/YM-uykVfq_E

Definition of entropy

- No clear definition but is approximately: **A measure of molecular disorder or molecular randomness of a system.**
- Entropy is abstract and difficult to give a physical description without considering the microscopic state of the system
- The second law of thermodynamics leads to the definition of the concept of “entropy”:

$$dS = \left(\frac{\delta Q}{T} \right)_{int\ rev} \quad unit: \left[\frac{kJ}{kg \cdot K} \right]$$

- “int rev” denotes entropy change is considered in an “internally reversible” path. E.g. a known constant temperature.
- Unlike energy, entropy is not conserved (no such thing as conservation of entropy). Hence the total entropy change (or generation) of a system is always +ve, i.e.:

$$\Delta S = (\Delta S_{system} + \Delta S_{surroundings}) \geq 0$$

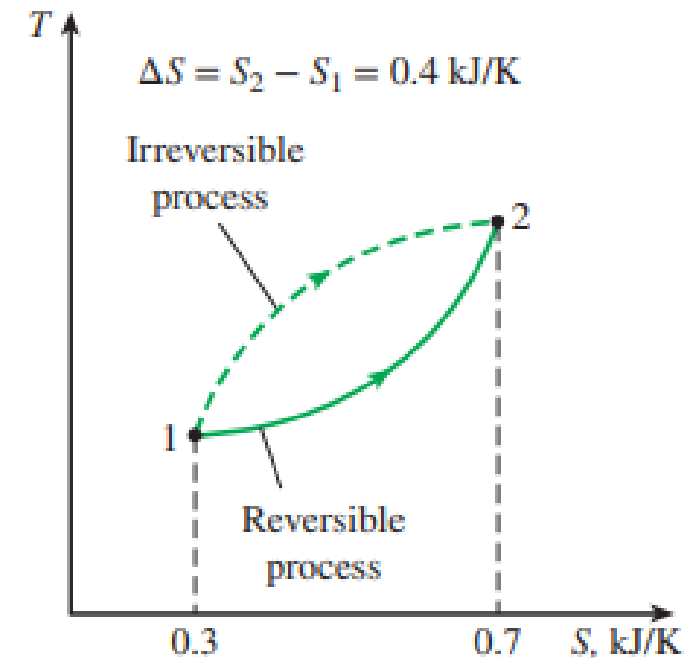
- Best understood and appreciated by studying its uses in commonly encountered engineering processes.

Evaluation of entropy – the concept of reversibility

- Entropy is central to the 2nd law of thermodynamics which tells us that no system, process or heat engine is 100% efficient (or 100% reversible), and the inefficiencies can be quantified by the change in this property.
- Consider the entropy change between two specified states 1 and 2 in the schematic:
- It is the same whether the process is reversible or irreversible
- Hence,

$$\Delta S = \oint \left(\frac{\delta Q}{T} \right)_{int rev} = \int_1^2 \left(\frac{\delta Q}{T} \right)_{int rev} = S_2 - S_1$$

- As engineers, we are more interested in the changes in entropy rather than absolute entropy values.
- To perform the integration, we need to know the relationship between Q & T during a process and is not always available. Hence the integration can only be done for a few simple cases.
- How do we then evaluate entropy??



Evaluation of entropy – isothermal systems

- Entropies of substances are evaluated from measurable property data rather than calculations, and are tabulated just like V, u, and h
- Entropy value of compressed liquid and superheated vapor regions are obtained directly from the tables at the specified state. In the saturated mixture region, it is determined from

$$s = s_f + x \cdot s_{fg} \text{ (kJ / kg} \cdot \text{K)}$$

where x is the quality and s_f and s_{fg} values are listed in the saturation tables.

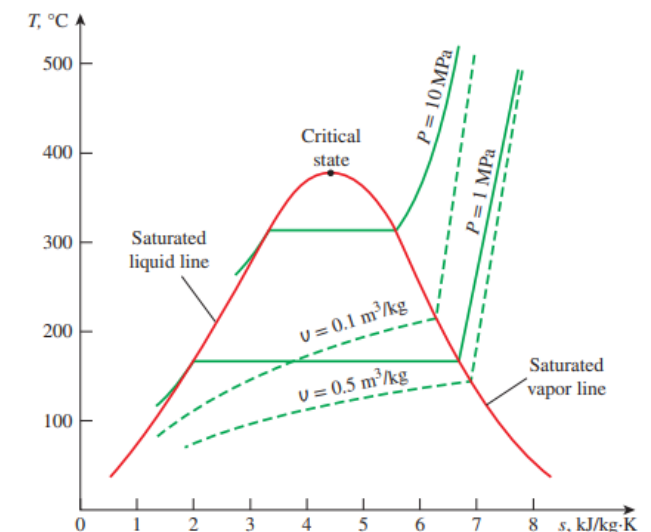
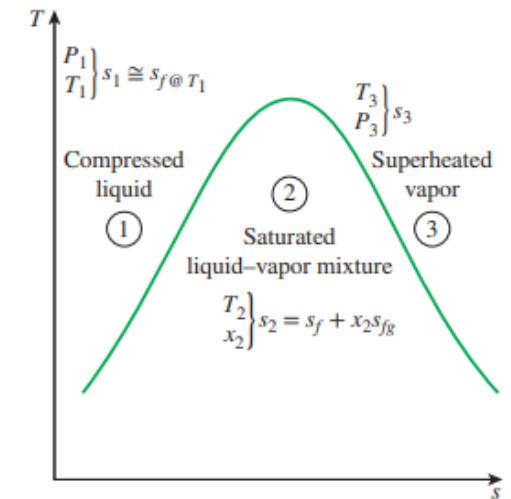
- In the absence of compressed liquid data, the entropy of the compressed liquid can be approximated by the entropy of the saturated liquid at the given temperature:

$$s @ T, P \cong s_f @ T \text{ (kJ / kg} \cdot \text{K)}$$

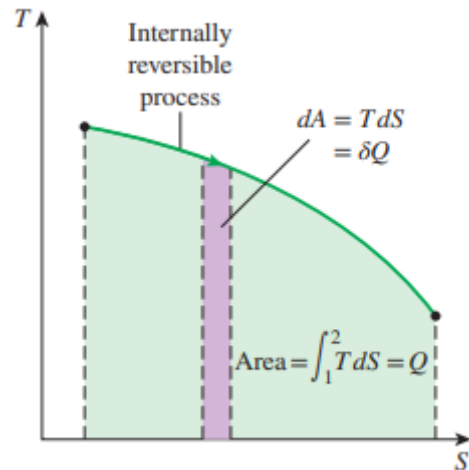
- The entropy change of a specified mass m (a closed system) during a process is simply

$$\Delta S = m \Delta s = m (s_2 - s_1) \text{ (kJ / K)}$$

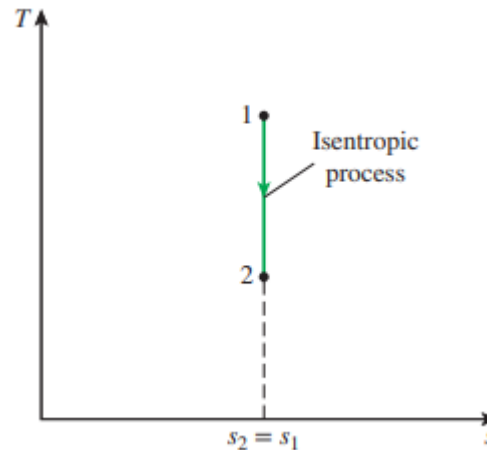
i.e. the difference between the entropy values at the final and initial states. Note S and s are in different units.



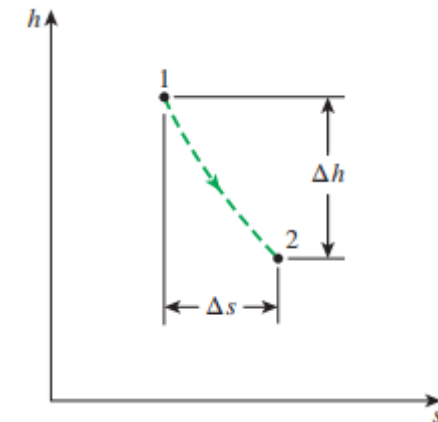
Evaluation of entropy – use of property diagrams



On a T-S diagram, the area under the process curve represents the heat transfer for internally reversible processes.



The isentropic process appears as a vertical line segment on a T-s diagram.



For adiabatic steady-flow devices, the vertical distance Δh on an h-s diagram is a measure of work, and the horizontal distance Δs is a measure of irreversibilities.

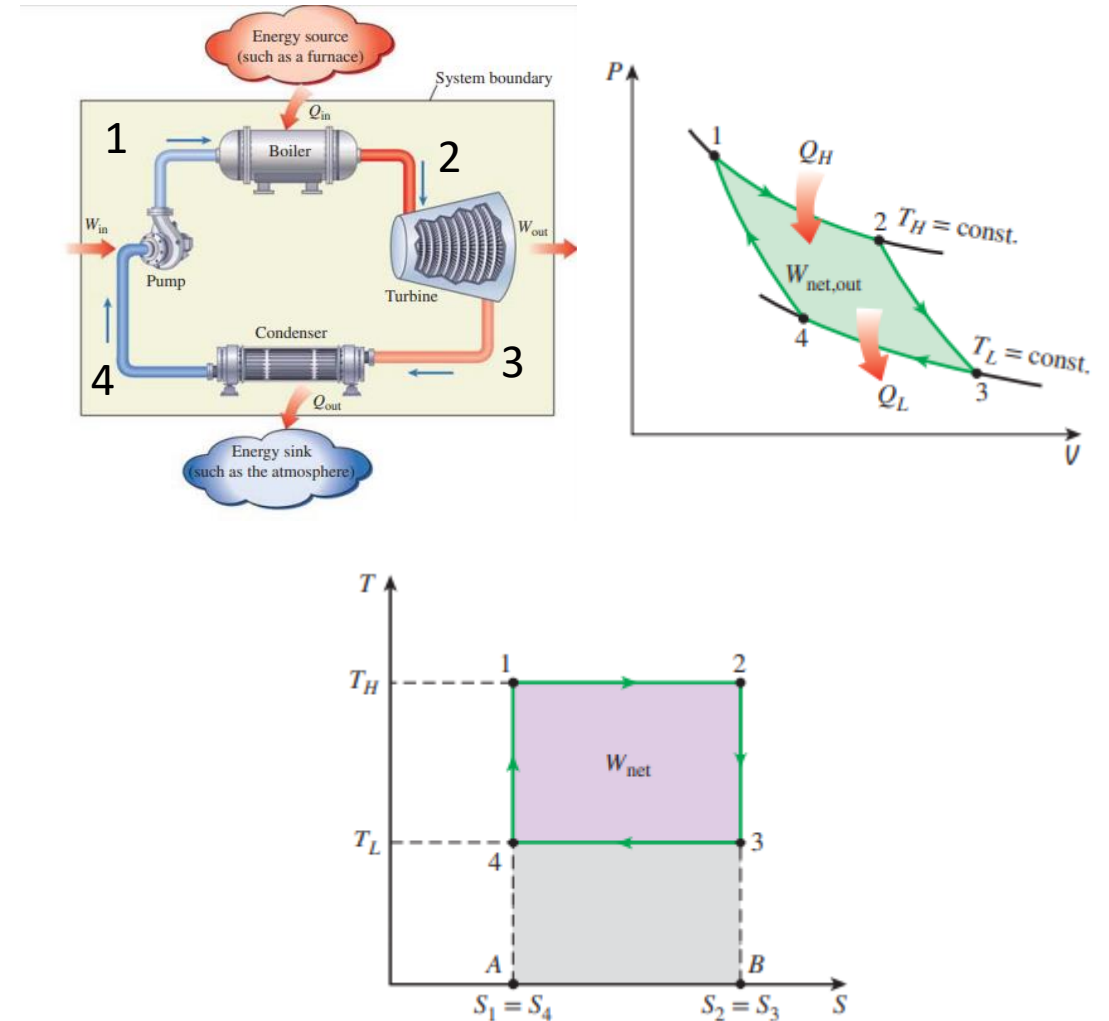
T-S diagram of the Carnot Cycle

- The Carnot cycle is made up of **two reversible isothermal** ($T = \text{constant}$) processes & **two isentropic** ($s = \text{constant}$) processes.
- These four processes form a rectangle on a T-S diagram (lower figure).
- On a T-S diagram, area under process curve represents the heat transfer for that process. Thus the area A12B represents Q_H , the area A43B represents Q_L , and the difference between these two (the area in colour) represents the net work since

$$W_{\text{net,out}} = Q_H - Q_L$$

Hence, the area enclosed by the path of a cycle (area 1234) on a T-S diagram represents the net work.

- The area enclosed by the path of a cycle also represents the net work on a P-V diagram.



Evaluation of entropy – isothermal systems

- The entropy change for a process, then, can be evaluated by integrating $\delta Q/T$ along an internally reversible path between the actual end states.
- For isothermal internally reversible processes, this integration is straightforward. Recall that:

$$\delta Q_{int\ rev} - \delta W_{int\ rev, out} = dU$$

- And

$$\begin{aligned}\delta Q_{int\ rev} &= TdS \\ \delta W_{int\ rev, out} &= PdV\end{aligned}$$

What happens when temperature changes?

Evaluation of non-isothermal entropy (Tds relationships)

Thus, $TdS = dU + PdV$ (kJ)

or

$Tds = du + PdV$ (kJ / kg) (i) {First TdS or Gibbs equation}

Differentiating the definition of enthalpy: $h = u + PV$ gives:

$$dh = du + PdV + VdP.$$

Now eliminating du using eqn (i) gives

$Tds = dh - VdP$ (ii) {2nd TdS equation}

Equations (i) and (ii) are extremely useful since they relate entropy changes of a system to changes in other properties of the system.

Evaluation of entropy – for liquids and solids

- For solids and liquids, volume is constant ($PdV = 0$). Equation (ii) becomes:

$$ds = \frac{du}{T} = \frac{C_v dT}{T}$$

- To obtain the entropy change between two states 1 and 2, we integrate the ds relationship above:

$$s_2 - s_1 = \int_1^2 ds = \int_1^2 \frac{c_v(T)dT}{T} \cong c_{avg} \ln \left(\frac{T_2}{T_1} \right) \quad \left[\frac{kJ}{kg \cdot K} \right]$$

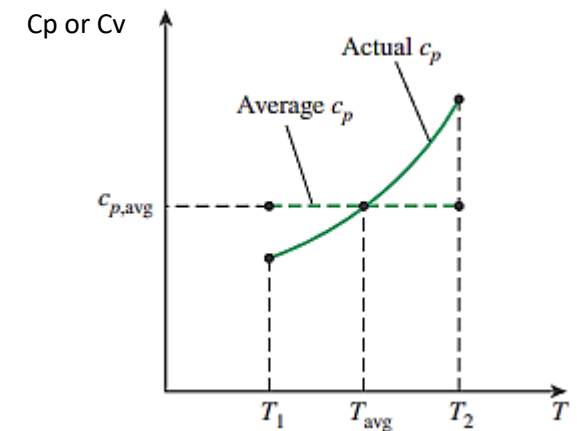
For isentropic processes,

$$s_2 - s_1 = 0$$

$$i.e., \quad c_{v,avg} \ln \left(\frac{T_2}{T_1} \right) = 0$$

Hence, for a truly incompressible substance, undergoing an isentropic processes

$$T_2 = T_1$$



Evaluation of entropy – ideal gas

- Back to our Tds relationships:

$$Tds = du + PdV$$

$$Tds = dh - VdP$$

For an ideal gas, substituting $P=RT/V$ and $V=RT/P$ respectively,

$$ds = \frac{du}{T} + \frac{RT}{V} \frac{dV}{T} \Rightarrow ds = c_v(T) \frac{dT}{T} + R \frac{dV}{V}$$

$$ds = \frac{dh}{T} + \frac{RT}{P} \frac{dP}{T} \Rightarrow ds = c_p(T) \frac{dT}{T} + R \frac{dP}{P}$$

Integrating both between states 1 and 2 as before, we obtain

$$s_2 - s_1 = c_{v,avg} \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{V_2}{V_1} \right)$$

$$s_2 - s_1 = c_{p,avg} \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{P_2}{P_1} \right)$$

Instead of integrating and trying to calculate $C_{v,avg}$ and $C_{p,avg}$ each time we have a new process, it is useful to define a new quantity s^o , the entropy at temperature T reference to the absolute zero temperature, hence: the equations above become:

$$s_2 - s_1 = s_2^o - s_1^o + R \ln \left(\frac{V_2}{V_1} \right) \left[\frac{\text{kJ}}{\text{kg} \cdot \text{K}} \right]$$

$$s_2 - s_1 = s_2^o - s_1^o - R \ln \left(\frac{P_2}{P_1} \right) \left[\frac{\text{kJ}}{\text{kg} \cdot \text{K}} \right]$$

Or

$$s_2 - s_1 = \bar{s}_2^o - \bar{s}_1^o + R_u \ln \left(\frac{V_2}{V_1} \right) \left[\frac{\text{kJ}}{\text{mol} \cdot \text{K}} \right]$$

$$s_2 - s_1 = \bar{s}_2^o - \bar{s}_1^o - R_u \ln \left(\frac{P_2}{P_1} \right) \left[\frac{\text{kJ}}{\text{mol} \cdot \text{K}} \right]$$

(See tables A17 – A25)

How do we use
entropy to our
advantage?



Isentropic processes

- These are ideal thermodynamic processes that are both adiabatic and reversible. As such, $s_2 - s_1 = 0$

$$\text{Hence, } s_2 - s_1 = c_{v,avg} \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{V_2}{V_1} \right) = 0$$

$$\ln \left(\frac{T_2}{T_1} \right) = -\frac{R}{c_v} \ln \left(\frac{V_2}{V_1} \right) \text{ assuming } c_v \text{ is constant}$$

$$\ln \left(\frac{T_2}{T_1} \right) = \ln \left(\frac{V_1}{V_2} \right)^{\frac{R}{c_v}} \Rightarrow \left(\frac{T_2}{T_1} \right) = \left(\frac{V_1}{V_2} \right)^{\frac{R}{c_v}}$$

Recall that $R = c_p - c_v$, if $k = c_p/c_v$, then $\frac{R}{c_v} = k - 1$

k is known as the isentropic index.

Hence:

$$\left(\frac{T_2}{T_1} \right)_{s=const.} = \left(\frac{V_1}{V_2} \right)^{k-1} \text{ \{first isentropic relationship\}}$$

- Note that it is valid for ideal gases assuming constant specific heat

- Similarly starting from $s_2 - s_1 = c_{p,avg} \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{P_2}{P_1} \right)$ for an ideal gas, it can also be shown that:

$$\left(\frac{T_2}{T_1} \right)_{s=const.} = \left(\frac{P_2}{P_1} \right)^{\frac{k-1}{k}} \text{ \{second isentropic relationship\}}$$

Eliminating the LHS in the 1st and 2nd isentropic relationships,

$$\left(\frac{P_2}{P_1} \right)_{s=const.} = \left(\frac{V_1}{V_2} \right)^k \text{ \{third isentropic relationship\}}$$

- In compact form,

$$\begin{aligned} TV^{k-1} &= \text{constant} \\ TP^{(1-k)/k} &= \text{constant} \\ PV^k &= \text{constant} \end{aligned}$$

Work done by a compressor or turbine

- This is defined as:

$$W_{rev} = \int_1^2 P dV \text{ (kJ/kg, closed system)}$$

$$W_{rev} = - \int_1^2 V dP - \Delta ke - \Delta pe \text{ (kJ/kg, flow system)}$$

Integrating,

$$\text{Closed system (at constant pressure): } W_{rev} = P(V_2 - V_1)$$

For a flowing, incompressible fluid,

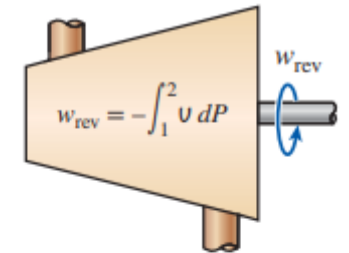
$$W_{rev} = -V(P_2 - P_1) - \frac{u_2^2 - u_1^2}{2} - g(z_2 - z_1)$$

Special case: when there is no work involved (e.g., pipe, valve, or nozzle),

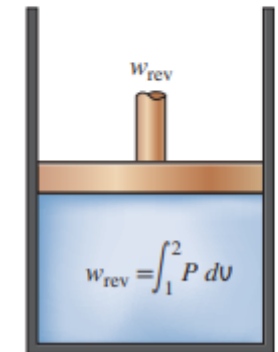
$$V(P_2 - P_1) + \frac{u_2^2 - u_1^2}{2} + g(z_2 - z_1) = 0$$

This is known as:

The Bernoulli equation



(a) Steady-flow system



(b) Closed system

Work done by a compressor or turbine – operating with an ideal gas

Substituting $PV=RT$, or PV^k in the work relationship on the last page,

- Isentropic (or adiabatic) – involves no cooling/heat transfer – ($PV^k = \text{constant}$):

$$w_{comp,in} = \frac{kR(T_2 - T_1)}{k - 1} = \frac{kRT_1}{k - 1} \left[\left(\frac{P_2}{P_1} \right)^{\frac{k-1}{k}} - 1 \right]$$

$$\text{where } k = c_p/c_v = \gamma$$

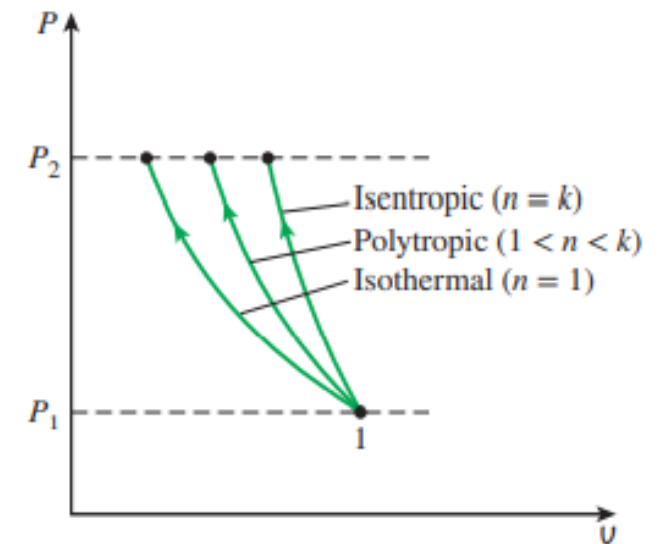
- Polytropic – involves some cooling or heat transfer – ($PV^n = \text{constant}$):

$$w_{comp,in} = \frac{nR(T_2 - T_1)}{n - 1} = \frac{nRT_1}{n - 1} \left[\left(\frac{P_2}{P_1} \right)^{\frac{n-1}{n}} - 1 \right]$$

$$\text{Where } 1 < n < k$$

- Isothermal – involves maximum cooling – ($PV = \text{constant}$)

$$w_{comp,in} = RT \ln \left(\frac{P_2}{P_1} \right)$$



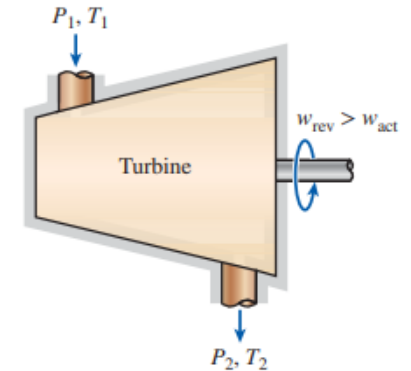
Proving these is left as an exercise

Variation of the polytropic index n

Polytropic index value	Relationship	Description
$n < 0$	—	Negative exponents describe processes having simultaneous work and heat flow in or out of the system. Without external forces except pressure, such spontaneous processes are not allowed by the second law of thermodynamics; however, negative exponents can be meaningful in some special cases not dominated by thermal interactions, such as in some chemical energy processes e.g. explosions.
$n = 0$	$p = C$	Equivalent to an isobaric process (constant pressure)
$n = 1$	$pV=C$	Equivalent to an isothermal process (constant temperature), under the assumption of ideal gas law, since then $pV=nRT$
$1 < n < \gamma$	—	Assuming ideal gas behaviour, heat and work flows go in opposite directions ($K > 0$), such as in vapor compression refrigeration during compression, where the elevated vapour temperature resulting from the work done by the compressor on the vapour leads to some heat loss from the vapour to the cooler surroundings.
$n = \gamma$	—	Equivalent to an isentropic process (adiabatic and reversible, no heat transfer), under the assumption of ideal gas law.
$\gamma < n < \infty$	—	Under the assumption of ideal gas law, heat and work flows go in the same direction ($K < 0$), such as in an internal combustion engine during the power stroke, where heat is lost from the hot combustion products, through the cylinder walls, to the cooler surroundings, at the same time as those hot combustion products push on the piston.
$n = +\infty$	$V=C$	Equivalent to an isochoric process (constant volume)

Minimising compressor work

- A reversible compressor uses less energy than an irreversible one if both operate between the same end states.
- How to minimise compressor work
 - Make process minimise friction, turbulence, and non-quasi-equilibrium compression
 - keeping the temperature of the gas as low as possible during compression since gas specific volume \propto temperature



Minimising compressor work

- Multistage compression with intercooling

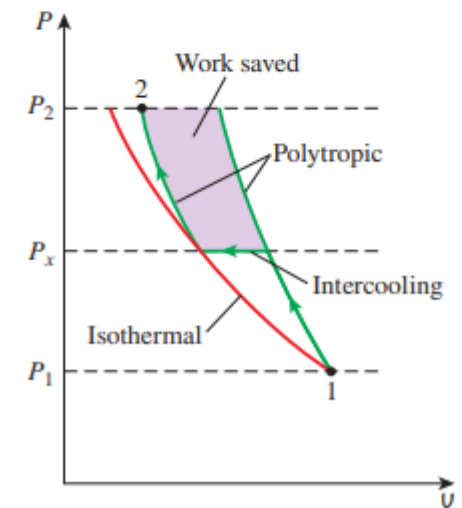
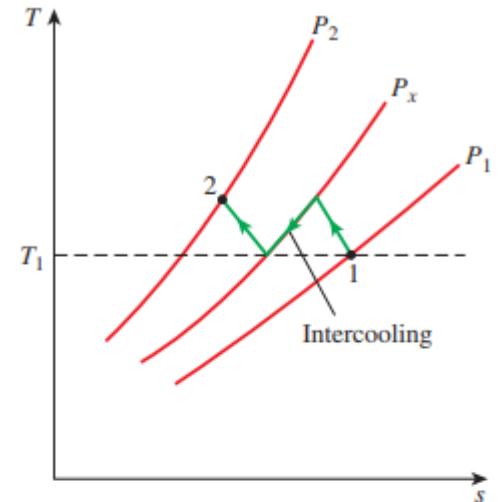
$$w_{comp,in} = \frac{nRT_1}{n-1} \left[\left(\frac{P_x}{P_1} \right)^{\frac{n-1}{n}} - 1 \right] + \frac{nRT_1}{n-1} \left[\left(\frac{P_2}{P_x} \right)^{\frac{n-1}{n}} - 1 \right]$$

Differentiating $w_{comp,in}$ wrt P_x , and equating to zero,

$$P_x = \sqrt{P_1 P_2} \quad \text{or} \quad \frac{P_x}{P_1} = \frac{P_2}{P_x}$$

Hence, to minimise $w_{comp,in}$ during two-stage compression, the pressure ratio across each stage must be equal. Therefore,

$$w_{comp,in,1} = w_{comp,in,2}$$



Isentropic efficiencies of steady flow devices - turbines

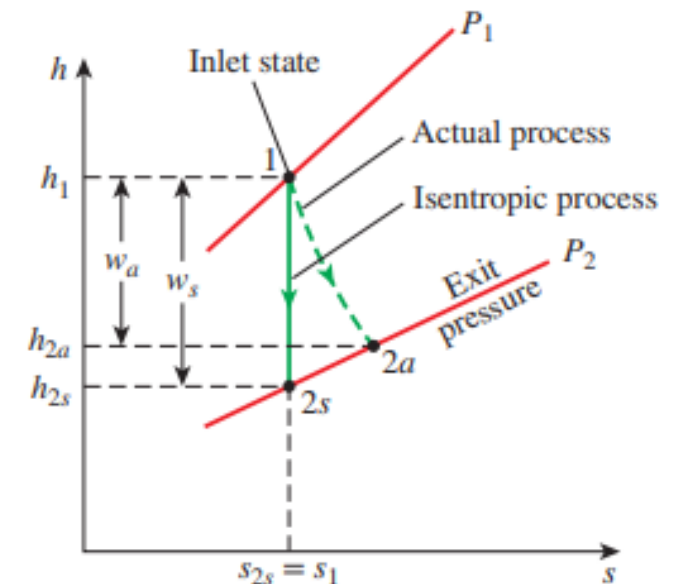
Isentropic efficiency of a turbine is defined as:

The ratio of the actual work output of the turbine to the work output achieved if the process between the inlet state and the exit pressure were isentropic:

$$\eta_T = \frac{\text{Actual turbine work}}{\text{isentropic turbine work}} = \frac{w_a}{w_s}$$

$$\eta_T \cong \frac{h_1 - h_{2a}}{h_1 - h_{2s}}$$

η_T ranges between 70 and 90%; and is determined by measuring w_a and calculating w_s for the measured inlet conditions and the exit pressure. This value is conveniently used for designing power plants.



Isentropic efficiencies of steady flow devices – pumps & compressors

Isentropic efficiency of a compressor is defined as:

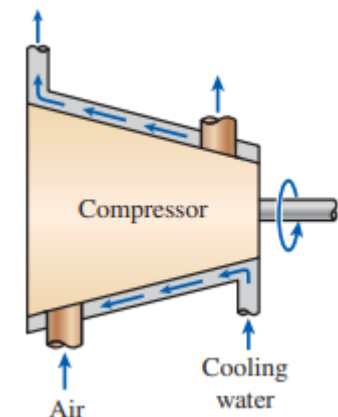
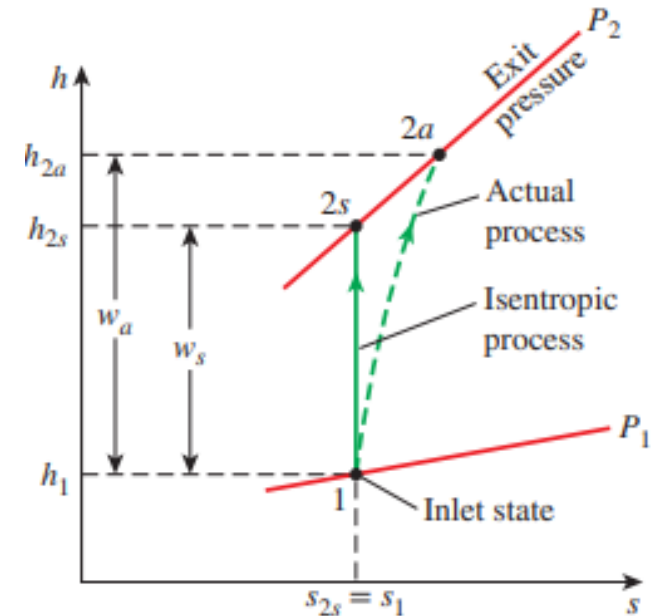
the ratio of the work input required to raise the pressure of a gas to a specified value in an isentropic manner to the actual work input:

$$\eta_c = \frac{\text{isentropic turbine work}}{\text{Actual turbine work}} = \frac{w_s}{w_a}$$

$$\eta_c \cong \frac{h_{2s} - h_1}{h_{2a} - h_1}$$

Again, as with turbines, η_c greatly depends on the compressor's design. Well-designed ones have $80\% < \eta_c < 90\%$.

What do we mean by “well-designed”?



Isentropic efficiencies of steady flow devices - nozzles

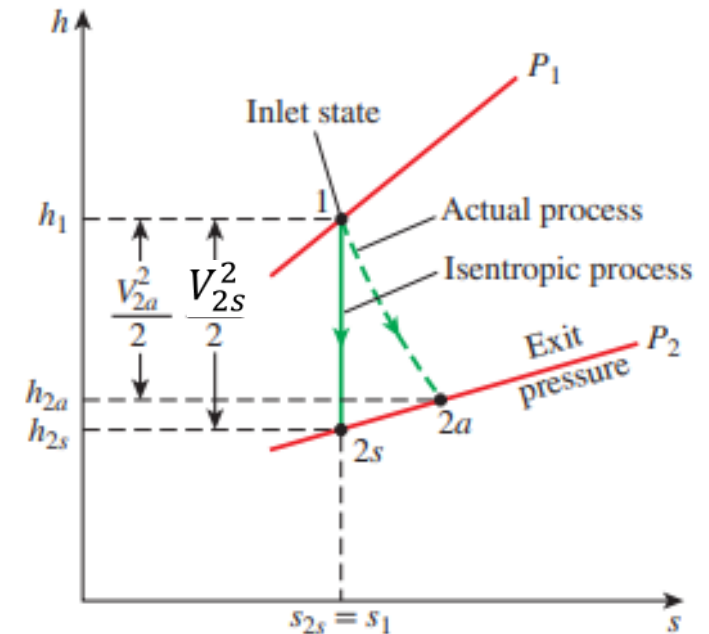
Isentropic efficiency of a nozzle is defined as:

the ratio of the actual kinetic energy of the fluid at the nozzle exit to the kinetic energy value at the exit of an isentropic nozzle for the same inlet state and exit pressure:

$$\eta_N = \frac{\text{Actual KE at nozzle exit}}{\text{Isentropic KE at nozzle exit}} = \frac{V_{2a}^2}{V_{2s}^2}$$

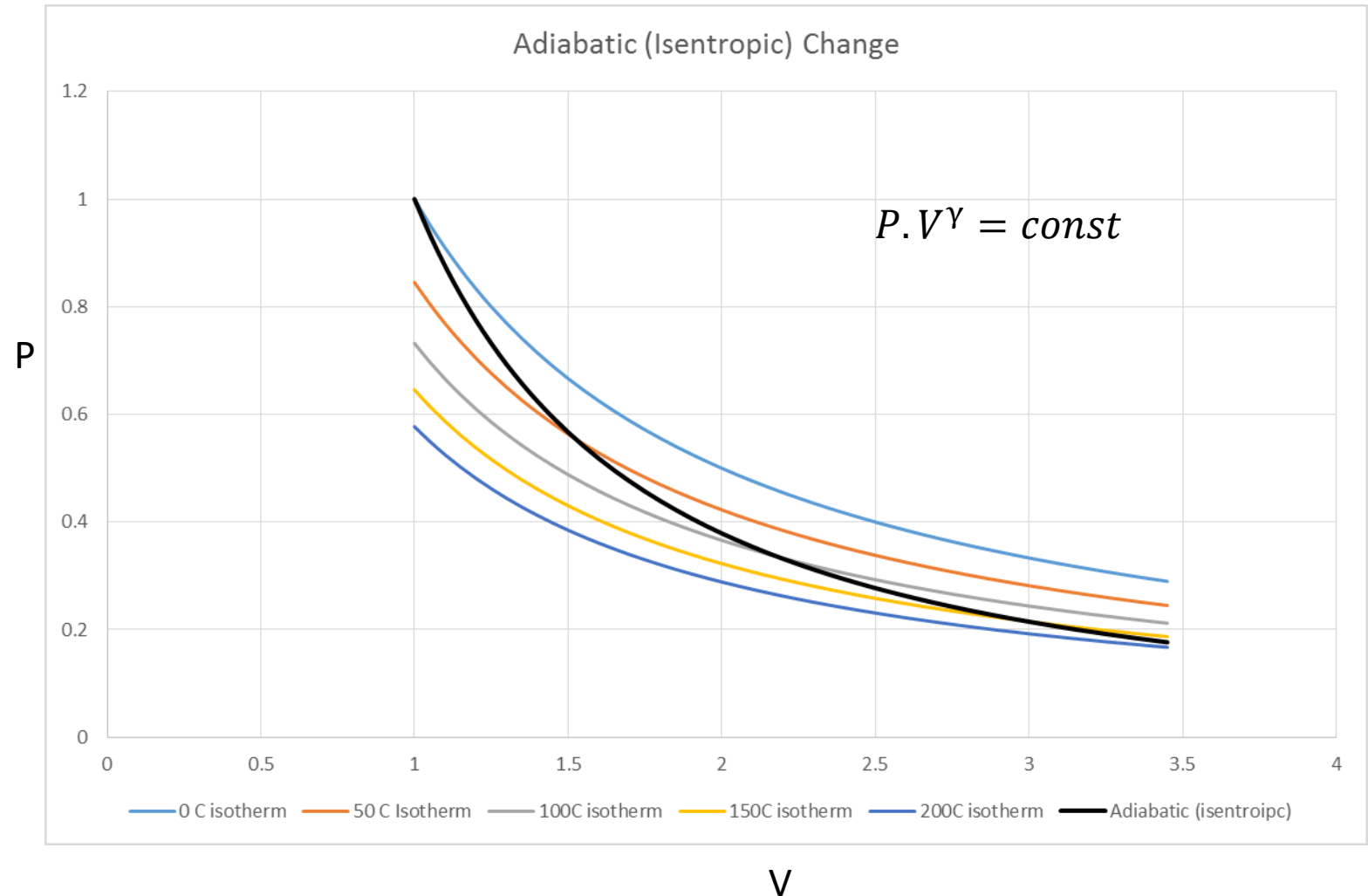
$$\eta_N \cong \frac{h_1 - h_{2a}}{h_1 - h_{2s}}$$

Isentropic efficiencies of nozzles are typically above 90%, and nozzle efficiencies > 95 percent are common



Adiabatic (Isentropic) Change of state

- This occurs if:-
- There is no loss of heat during the compression or expansion ie
- Change is made sufficiently quickly
- Change is made with “perfect” thermal insulation



Summary

- Constant Temperature $P_1 V_1 = P_2 V_2$
- Constant Pressure $V_1/T_1 = V_2/T_2$
- Constant Volume $P_1/T_1 = P_2/T_2$
- Combined $P.V=n.R.T$ or if R is gas specific $P.V=m.R.T$ where m=mass
- Isentropic $P.V^\gamma = \text{const}$
- Isentropic Volume ratio compression $T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma-1}$
- Isentropic Pressure ratio compression $T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$
- $C_p = C_v + R$
- Entropy $\Delta S = \int_i^f dQ/T = n C_v \ln\left(\frac{T_f}{T_i}\right) + n R \ln\left(\frac{V_f}{V_i}\right)$ for an ideal gas
- Carnot efficiency $\text{Eff} = 1 - \frac{T_c}{T_h}$
- Thermal efficiency $\eta_{th} = \frac{W_{net}}{Q_{in}}$

Recap

- Revision of the gas laws
- Entropy
- Entropy property diagrams (for Carnot Cycle)
- Evaluation of entropy for ideal gases, liquids, solids
- Evaluation of entropy for isothermal/non-isothermal processes
- Isentropic processes
 - For pumps/compressors
 - Turbines
 - Nozzles