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Applied Thermodynamics

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Adapted from: Y.A. Cengel, M. A. Boles, Thermodynamics – An Engineering Approach (5th Edition)

Chapter 7

Entropy

Entropy

- The second law of thermodynamics is closely associated to **inequalities**. For example, the efficiency of an irreversible heat engine is lower than that of a reversible engine operating between the same thermal resevoirs.
- Another example is given by the **Clausius inequality** (which can be demonstrated using the Kelvin-Planck statement):

$$\oint \frac{\delta Q}{T} \leq 0$$

- The integral symbol means that the integral is performed over the whole cycle
- This relation is valid for all cycles, wether reversible or not!
- In the case of a reversible cycle, we have:

$$\oint \left(\frac{\delta Q}{T}\right)_{rev,int} = 0$$

Entropy

- This last case (reversible cycle) is particularly interesting since a cyclic integral equal to zero is null if this integral does not depend on the process, but only on the **system state**. In this case, the quantity within the integral is a **property**.
- This new property is called **Entropy:**

$$dS = \left(\frac{\delta Q}{T}\right)_{rev,int}$$

- Since entropy is a state variable, the variation of entropy between two states is independent on the followed path, wether the process is reversible or not.
- To calculate the entropy variation of a system, we need to integrate the above expression between the initial and final states, taking the case of a reversible process:

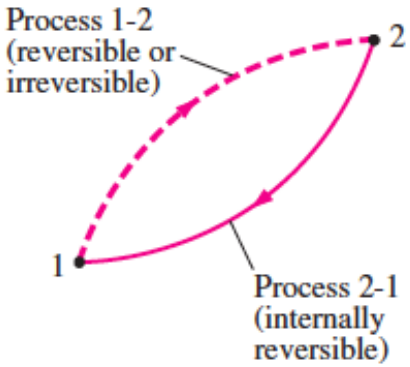
$$\Delta S = S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T}\right)_{rev,int}$$

The increase of entropy principle

- Let's consider a cycle composed of a reversible process from state 2 to state 1 and an irreversible process from state 1 to state 2:

$$\int_1^2 \frac{\delta Q}{T} + \int_2^1 \left(\frac{\delta Q}{T}\right)_{rev,int} \leq 0$$

$$\Leftrightarrow S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$$



- The strict inequality corresponds to an irreversible process. In that case, the inequality can be re-written as an equality by using an additional **entropy generation** term, which is always positive:

$$\Delta S_{sys} = S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + S_{gen}$$

- The first term of the right-hand side is the **entropy transfer** via heat: it is the entropy increase brought by the heat transfer if the system is reversible (S_{gen}=0)

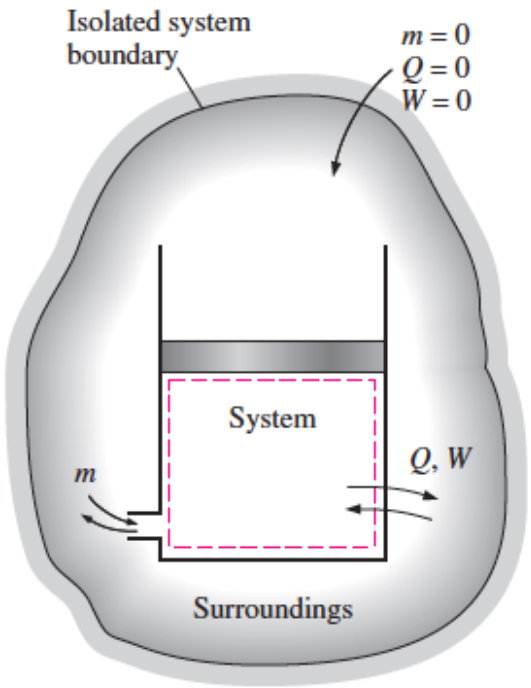
The increase of entropy principle

- In the case of an isolated system (no energy or mass transfer), the variation of entropy is equal to the generation of entropy:

$$\Delta S_{isolated} = S_{gen} \geq 0$$

The entropy of an isolated system during a process always increases or, in the limiting case of a reversible process, remains constant.

In other words: **The entropy of an isolated system never decreases.**



- If we consider a system together with its surroundings (=**Universe**), we can consider this new system as isolated. Therefore:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = S_{gen} \geq 0$$

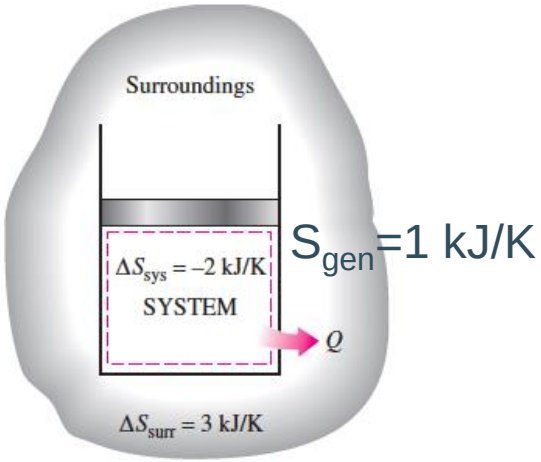
- Since no process is completely reversible, **the entropy of the universe is continuously increasin**g.

The increase of entropy principle

- The increase of entropy principle can be summarized by:

$$S_{gen} \begin{cases} > 0 & irreversible\ process \\ = 0 & reversible\ process \\ < 0 & impossible\ process \end{cases}$$

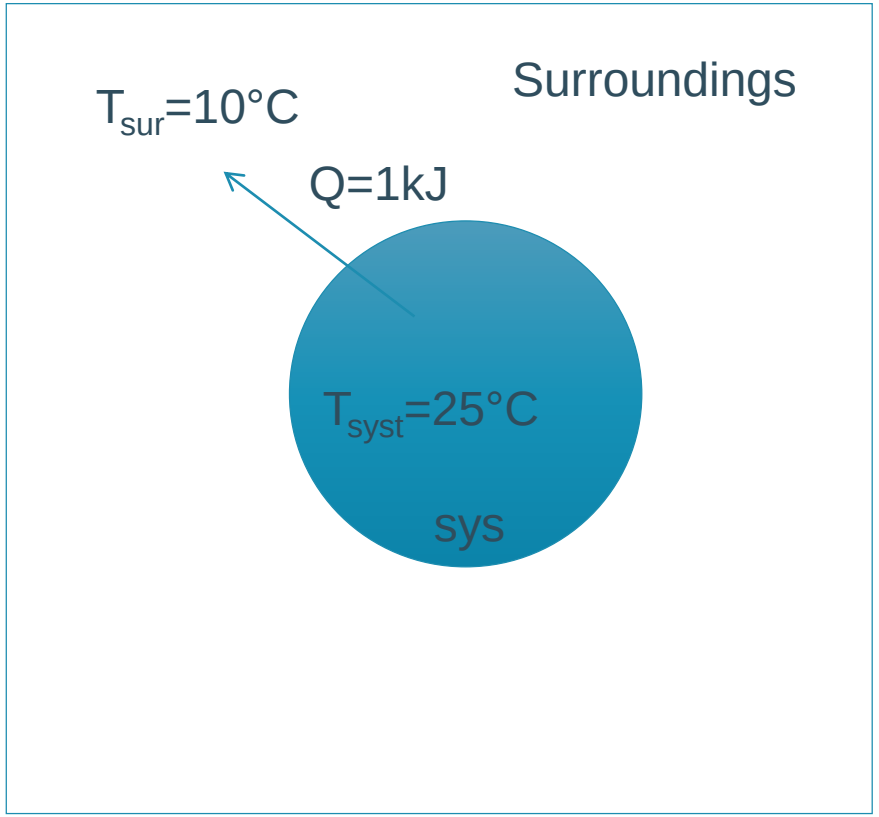
- Entropy generation is not a state function since it depends on the process path
- NB: entropy variation within a system can be negative, but entropy generation can never be negative!



S_{gen}=1 kJ/K

$S_{gen} = \Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = 1$ kJ/K

The increase of entropy principle



$$\Delta S_{sys} = \int_1^2 \frac{\delta Q}{T} + S_{gen,sys} = \frac{Q}{T_{sys}} = \frac{-1}{25+273}$$

$$\Delta S_{sur} = \int_1^2 \frac{\delta Q}{T} + S_{gen,sur} = \frac{Q}{T_{sur}} = \frac{1}{10+273}$$

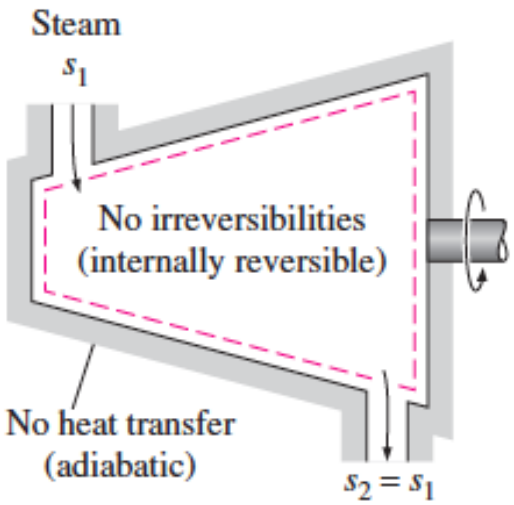
$$S_{gen,univ} = \Delta S_{sur} + \Delta S_{sys}$$

The increase of entropy principle

- Processes can occur in a certain direction only, the one that complies with the increase of entropy principle ($S_{gen}>0$)
- Entropy is a non conserved property, except in the case of reversible evolution. There is no such thing as the conservation of entropy principle.
- Entropy generation is a measure of the magnitudes of irreversibilities. The greater the irreversibilities, the greater the entropy generation.

Isentropic processes

$$\Delta S_{sys} = S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + S_{gen}$$



- According to the above equation, the entropy of a substances varies if:
  - This substance receives heat
  - Irreversibilities are generated internally.

⇒ If the system is adiabatic and if the process is internally reversible, the entropy does not change. The process is **isentropic**.

$$\Delta s = s_2 - s_1 = 0$$

- Pumps, compressors and turbines are nearly adiabatic. In these components the performance is maximized if the irreversibilities (e.g. friction) are minimized.
- Therefore, the isentropic case can be selected as reference case to which real processes can be compared.

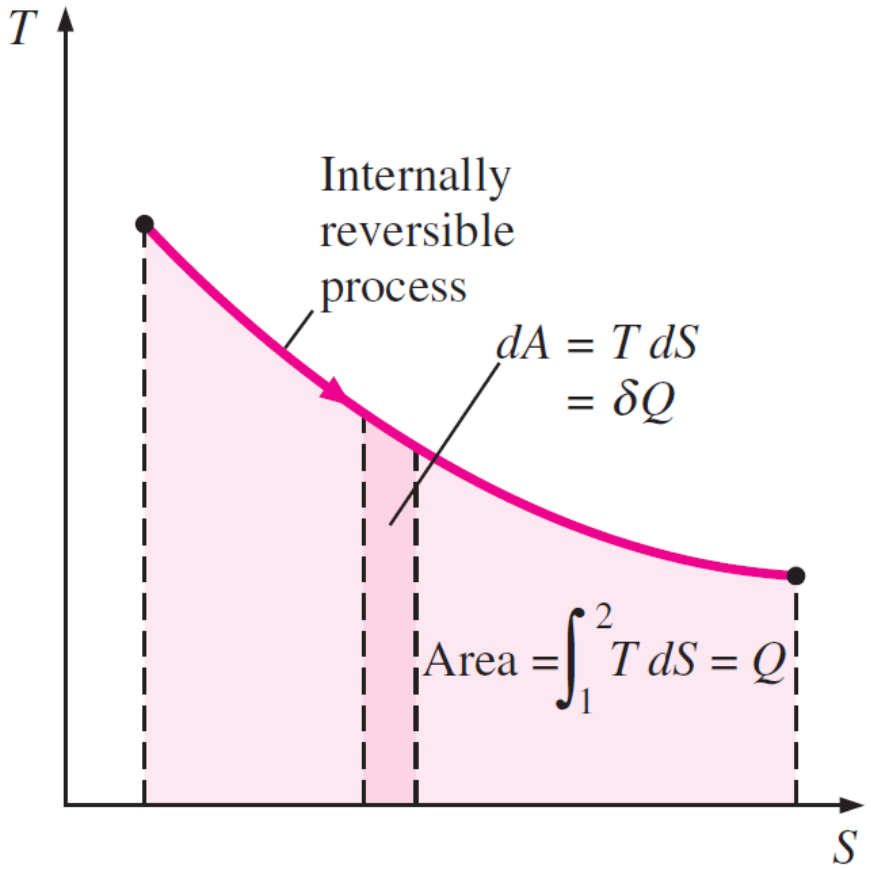
Property diagrams involving entropy

- From the definition of entropy:

$$\delta Q_{\text{int rev}} = T\ dS$$

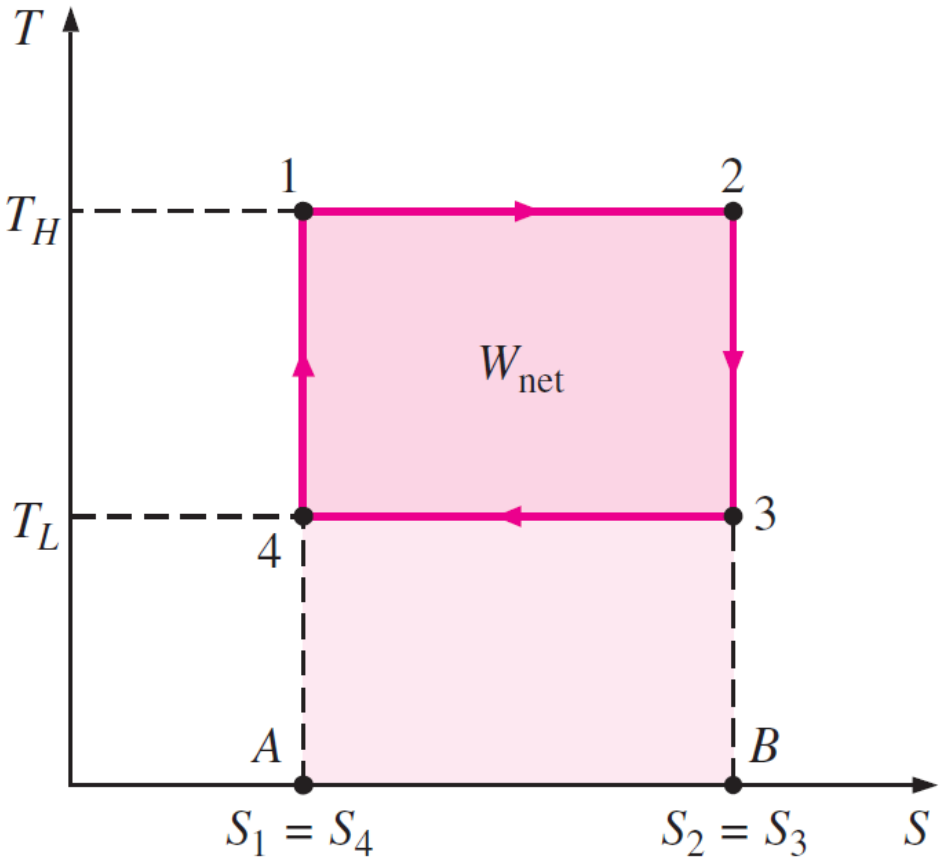
- Therefore, the area under the process curve on a T-S diagram represents heat transfer during an internally reversible process
- Particular case: isothermal heat transfer:

$$Q_{\text{int rev}} = T_0\ \Delta S$$



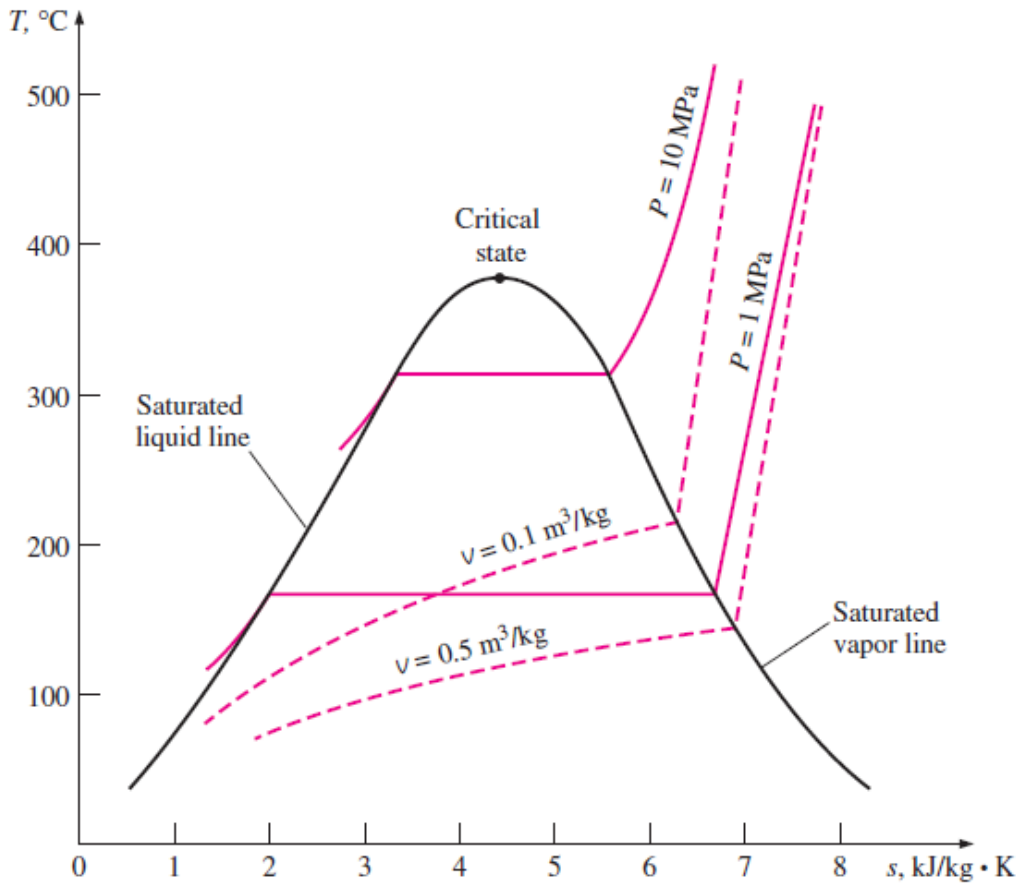
The Carnot cycle in the T-s diagram

- The T-s diagram is useful to visualize irreversibilities in a cycle
- Adiabatic reversible compression and expansion are isentropic. They appear as vertical lines
- Isothermal processes appear as horizontal lines



The T-s diagram of water

- As in the p-V diagram we can draw the liquid and vaport saturation lines in the T-s diagram.
- The vapor zone corresponds to high entropy values.
- Entropy can be viewed as a measure of molecular disorder, or molecular randomness: it is higher in vapor state than in liquid state



The T ds relations

Gibbs equation

- In a process the variation of entropy of a system can be evaluated by considering a reversible process between the initial and the final states:

$$\delta Q_{rév,int} = T\ dS$$

- If we consider a closed system undergoing an internally reversible process, the differential equation of the energy balance (first law of thermodynamics) is written:

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

- But we also know that the reversible work is given by:

$$\delta W_{rév,int} = P\ dV$$

And therefore: $$\boldsymbol{T\ ds = du + P\ dv}$$

Since h=u+pv, we also have: $$\boldsymbol{T\ ds = dh - v\ dP}$$

The equations allow calculating the entropy variation of a systems as a function of the variations of other thermodynamic variables. They are independent of the process path (reversible or irreversible) and can be applied to open or closed systems

Variation of entropy in the case of ideal gases

- To express the entropy variation of an ideal gas, we substitute $du=c_v dT$ and $P=RT/V$ in the first Gibbs equation.

$$s_2 - s_1 = \int_1^2 c_v(T)\frac{dT}{T} + R\ln\frac{v_2}{v_1}$$

- If enthalpy is considered (e.g. for an open system), we take the second equation and substitute $dh=c_p dT$

$$s_2 - s_1 = \int_1^2 c_p(T)\frac{dT}{T} - R\ln\frac{P_2}{P_1}$$

Variation of entropy in the case of ideal gases

Particular case of perfect gases

- In the case of a perfect gas (c_p and c_v are constant), if the evolution is isentropic:

$$\ln\frac{T_2}{T_1} = \ln\left(\frac{v_1}{v_2}\right)^{\frac{R}{c_v}}$$

$$\Leftrightarrow \left(\frac{T_2}{T_1}\right)_{s=constant} = \left(\frac{v_1}{v_2}\right)^{k-1}$$

- In the same manner:

$$\left(\frac{T_2}{T_1}\right)_{s=constant} = \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}}$$

- By combining both equation, we also have:

$$\left(\frac{P_2}{P_1}\right)_{s=constant} = \left(\frac{v_1}{v_2}\right)^{k}$$

Variation of entropy in the case of ideal gases

Particular case of perfect gases

- The above equations can be shortened into:

$$T\,v^{k-1} = constant$$
$$T\,P^{\frac{1-k}{k}} = constant$$
$$P\,v^{k} = constant$$

- Which corresponds to a particular case of polytropic process with n=k

Work of steady-flow reversible process

The first law of thermodynamics applied to a steady-flow process in the reversible is written:

$$\delta q_{rev} - \delta w_{rev} = dh + dk_e + dp_e$$

We also know that, by definition:

$$\delta q_{rev} = T\ ds\ and\ T\ ds = dh - v\ dP$$

Therefore:

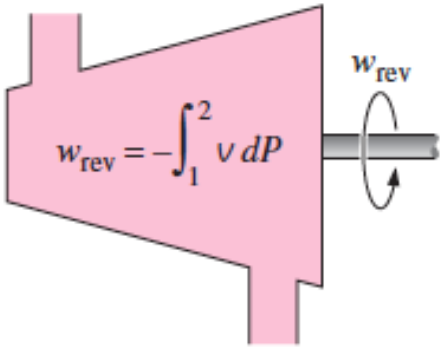
$$w_{rev} = -\int_1^2 v\ dP - \Delta k_e - \Delta p_e\ \ (J/kg)$$

If the variations of kinetic and potential energy are neglected, we finally obtain:

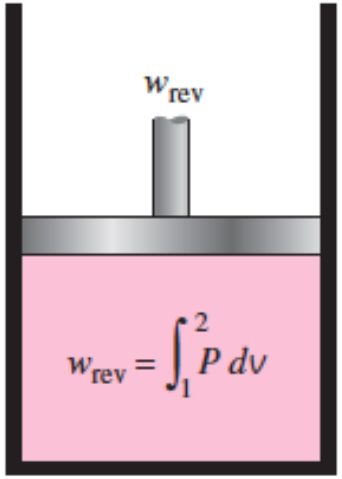
$$w_{rev} = -\int_1^2 v\ dP\ \ (J/kg)$$

And if the fluid is incompressible:

$$w_{rev} = -v(P_2 - P_1)\ (J/kg)$$



(*a*) Steady-flow system



(*b*) Closed system

Minimizing compression work

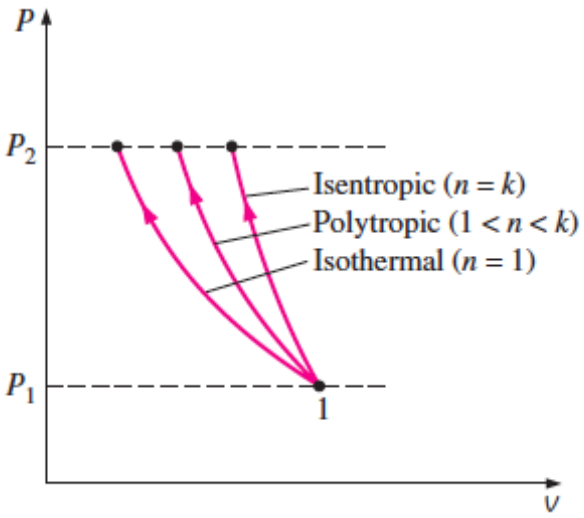
To minimize the compression work we can:

- reduce irreversibilities (friction, turbulence)
- Reduce the specific volume of the gas during the comrpession:

$$w_{rev,in} = -\int_1^2 v\, dP \;\; (J/kg)$$

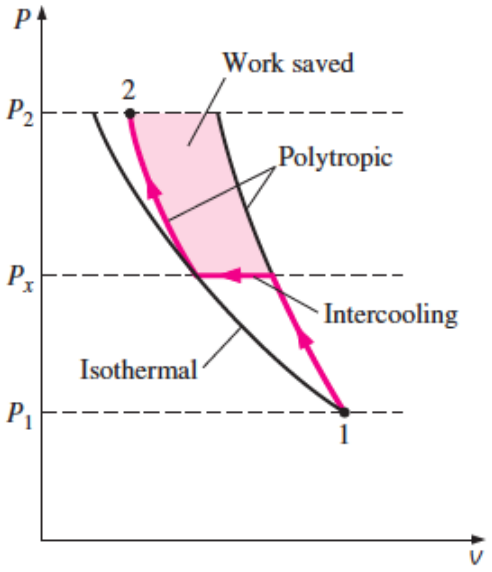
To reduce the specific volume of the gas, it is necessary to cool it down.

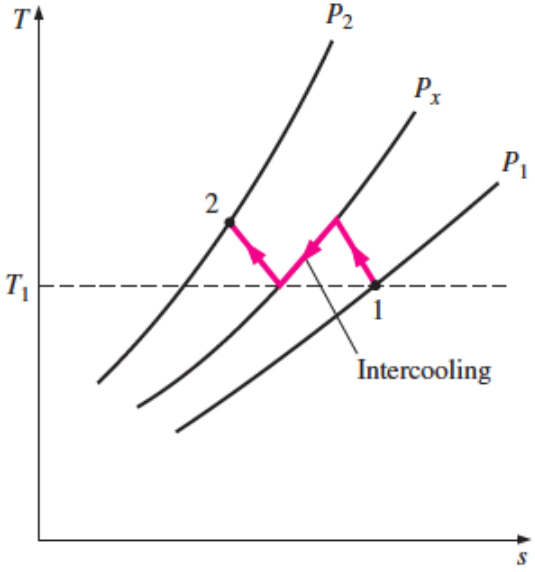
The compression work is minimal in the case of an isothermal compression (P v=constant)

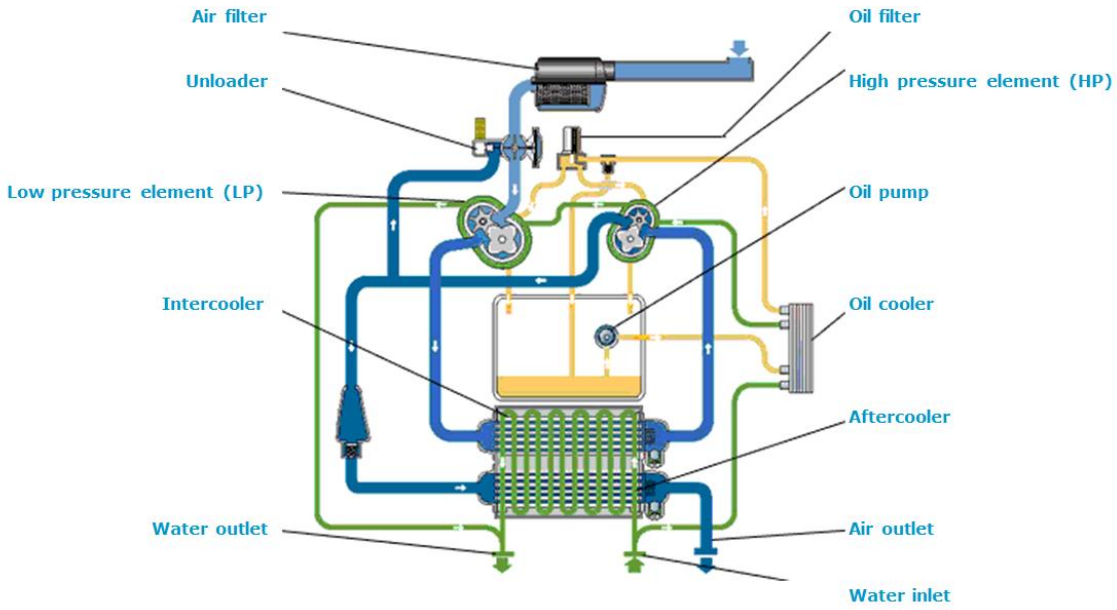


Minimizing compression work

- In practice, it is not possible to create a perfectly isothermal compression
- A two-stage or multi-stage compression is considered insteead
- The compression is stopped and inter-cooling is added before the next compression stage





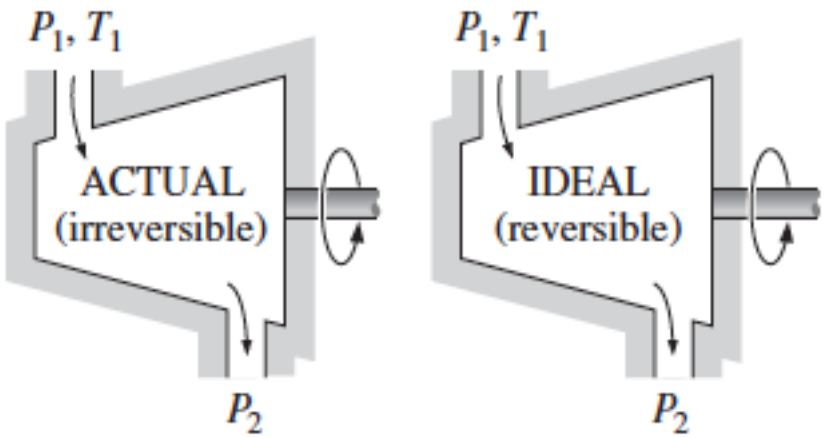


Isentropic efficiency of steady-flow devices

- Irreversibilities downgrade the performance of devices.

In the previous chapter, we expressed the performance of cycle by its thermal efficiency. In this chapter, we would like to find a performance indicator for devices working under steady-flow conditions.

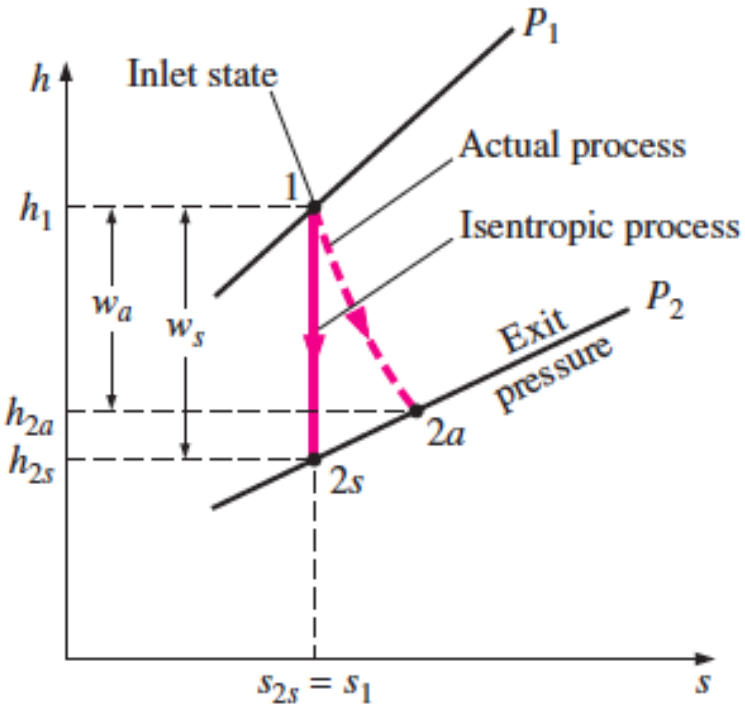
For that purpose, we select an ideal case: an internally reversible and adiabatic process, i.e. isentropic. We are going to compare the actual proces agains this ideal process.



NB: An isentropic evolution is not necessarily reversible since entropy generation through irreversibilities can be exactly compensated by entropy losses linked to a heat transfer with the surroundings.

Isentropic efficiency of turbines

The isentropic efficiency is defined by the ratio between actual work output and the work that would be produced if the turbine was adiabatic and reversible (=> isentropic)



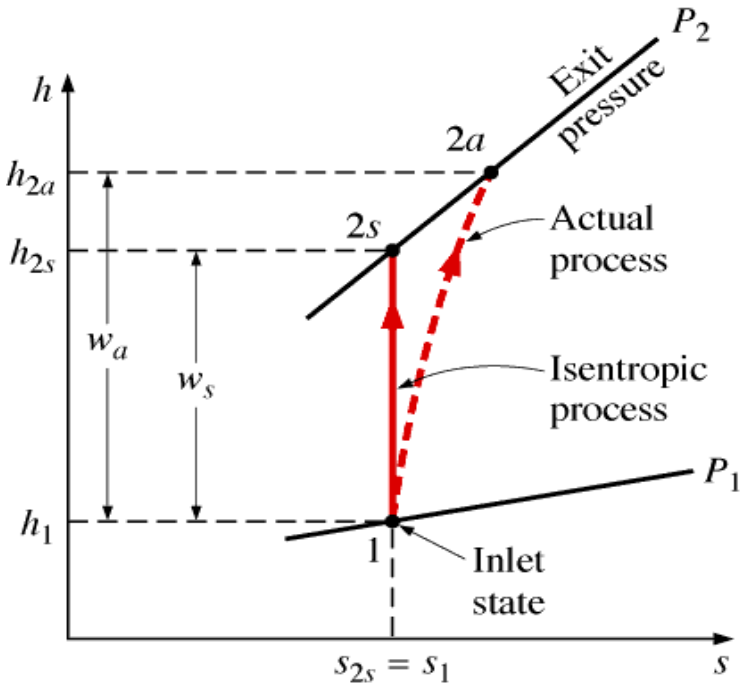
$$\varepsilon_{s,turbine} = \frac{w_a}{w_s}$$

If the actual process is adiabatic:

$$\varepsilon_{s,turbine} = \frac{h_1 - h_{2,a}}{h_1 - h_{2,s}}$$

Isentropic efficiency of compressors

In the actual case, the work required for the compression is higher than in the ideal (isentropic) case. The isentropic efficiency is thus defined as the ratio between the ideal work (numerator) and the actual work (denominator).



If the actual process is adiabatic:

$$\varepsilon_{s,compressor} = \frac{h_{2,s} - h_1}{h_{2,a} - h_1}$$

In the particular case of pump (incompressible fluid), the isentropic compression can be expressed directly in terms of v and p:

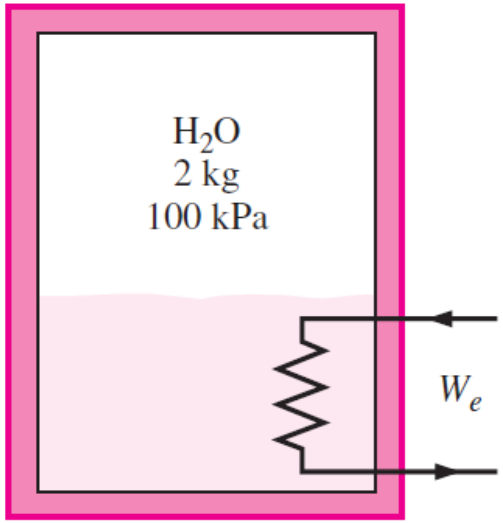
$$\varepsilon_{s,pump} = \frac{v\,(p_2 - p_1)}{h_2 - h_{1,a}}$$

Exercises in EES

7–29 Refrigerant-134a enters the coils of the evaporator of a refrigeration system as a saturated liquid–vapor mixture at a pressure of 160 kPa. The refrigerant absorbs 180 kJ of heat from the cooled space, which is maintained at −5°C, and leaves as saturated vapor at the same pressure. Determine (*a*) the entropy change of the refrigerant, (*b*) the entropy change of the cooled space, and (*c*) the total entropy change for this process.

Exercises in EES

7–34 A well-insulated rigid tank contains 2 kg of a saturated liquid–vapor mixture of water at 100 kPa. Initially, three-quarters of the mass is in the liquid phase. An electric resistance heater placed in the tank is now turned on and kept on until all the liquid in the tank is vaporized. Determine the entropy change of the steam during this process. *Answer:* 8.10 kJ/K

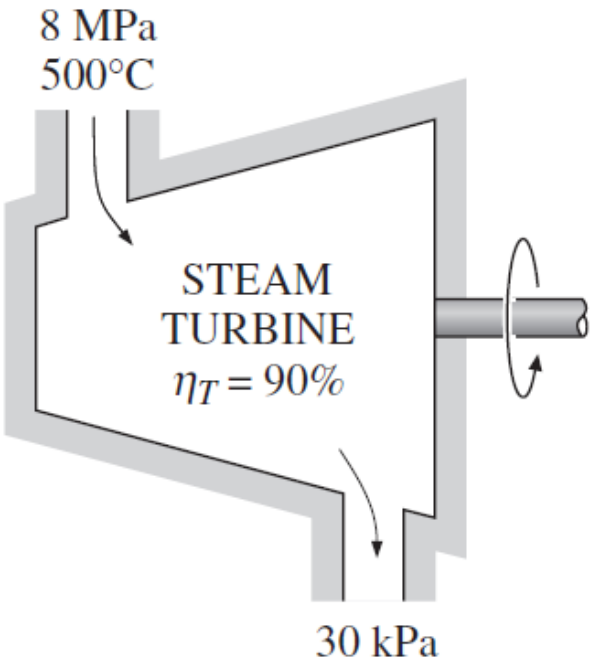


Exercises in EES

7–41 Refrigerant-134a enters an adiabatic compressor as saturated vapor at 160 kPa at a rate of 2 m^3/min and is compressed to a pressure of 900 kPa. Determine the minimum power that must be supplied to the compressor.

Exercises in EES

7–75 Air is compressed in a piston–cylinder device from 100 kPa and 17°C to 800 kPa in a reversible, adiabatic process. Determine the final temperature and the work done during this process, assuming (*a*) constant specific heats and (*b*) variable specific heats for air. *Answers:* (*a*) 525.3 K, 171.1 kJ/kg, (*b*) 522.4 K, 169.3 kJ/kg

Exercises in EES

7–104 Steam enters an adiabatic turbine at 8 MPa and 500°C with a mass flow rate of 3 kg/s and leaves at 30 kPa. The isentropic efficiency of the turbine is 0.90. Neglecting the kinetic energy change of the steam, determine (*a*) the temperature at the turbine exit and (*b*) the power output of the turbine. *Answers:* (*a*) 69.1°C, (*b*) 3054 kW