

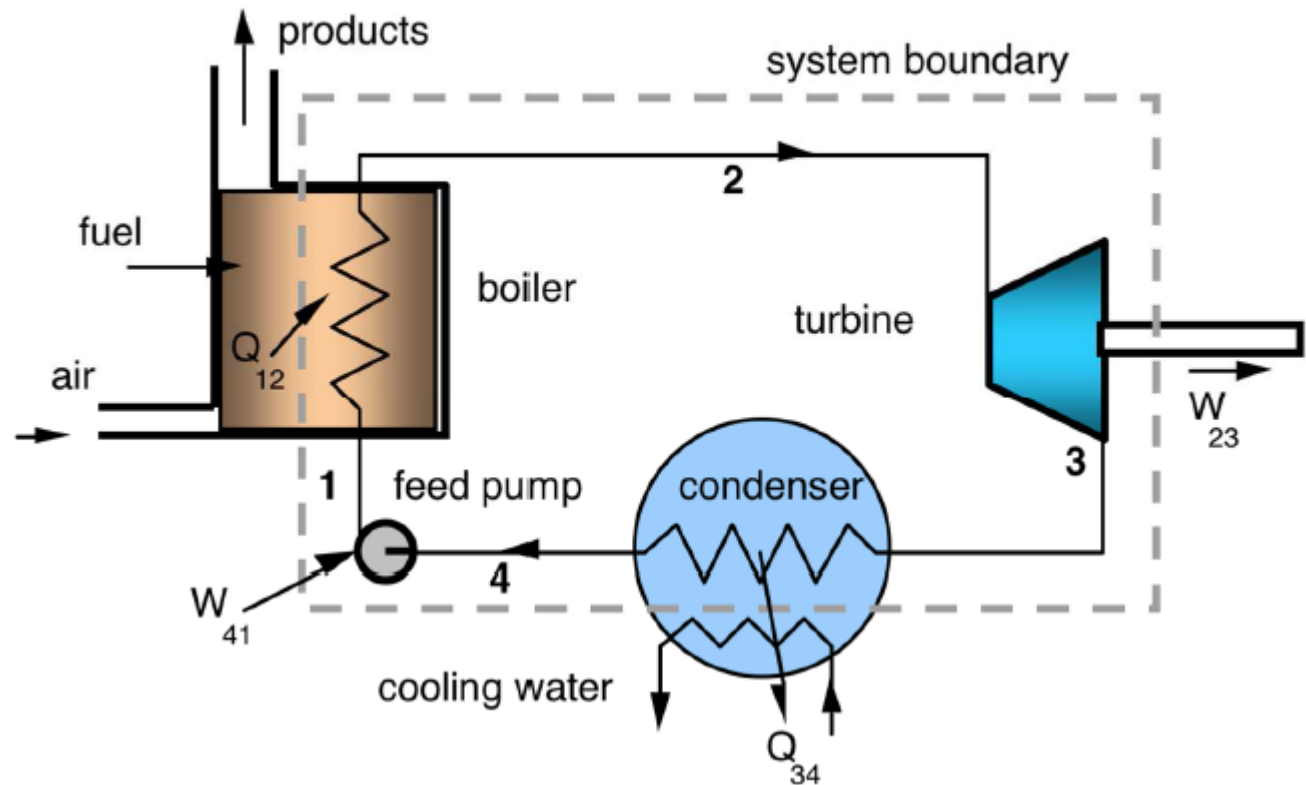
Second Law of Thermodynamics

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- Heat engines, heat work and energy
- Reversed heat engines
- The 2nd Law of Thermodynamics
- Reversibility and irreversibility
- The Carnot engine and Carnot cycle
- Thermodynamic temperature scale
- Entropy, T-s diagram, increase of entropy and Clausius inequality
- Entropy generation
- Entropy change for ideal gases
- Isentropic efficiency
- Exergy and 2nd Law efficiency

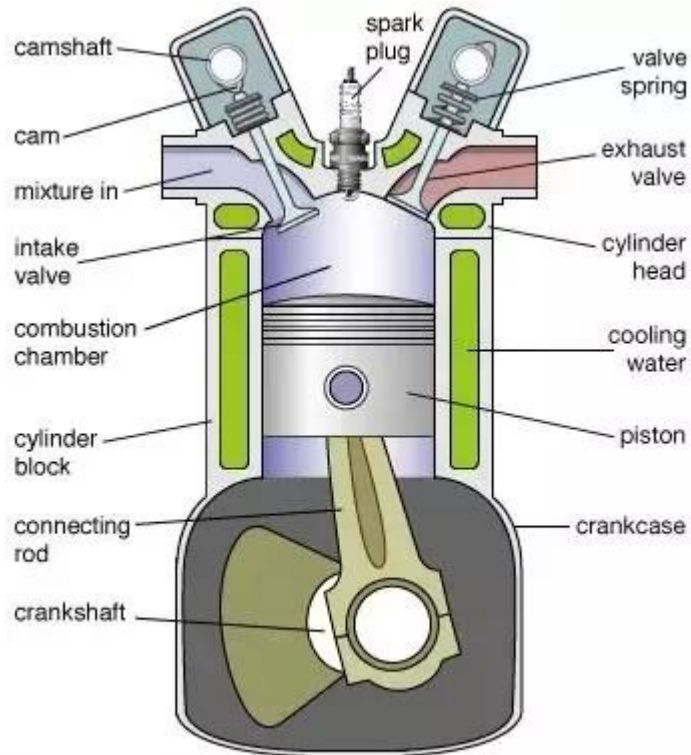
Heat engines

Steam plant

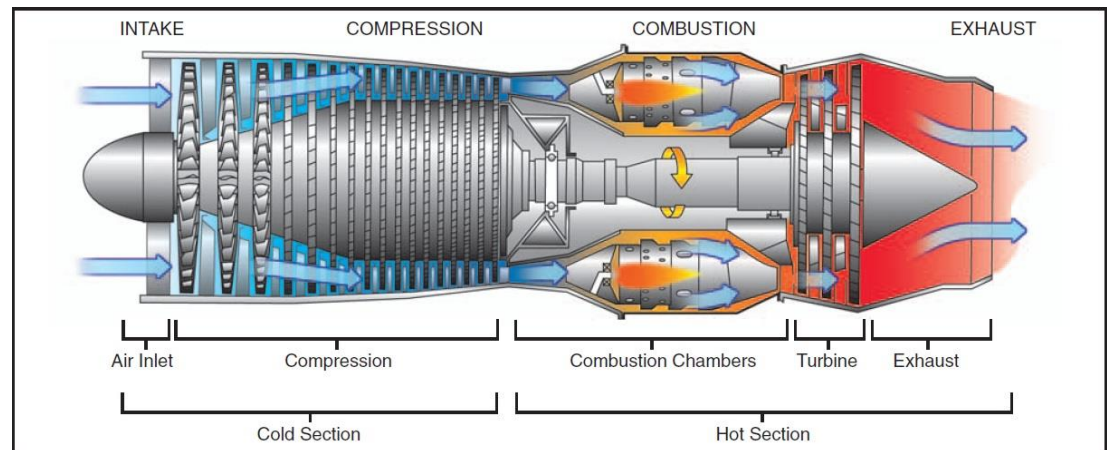


A heat engine is a device which operates in a cycle with only **heat transfer** and **work transfer** crossing the system boundary.

Other types of engines



Internal combustion engines



Gas turbine engines

When the Watt steam engine of 1776 was installed to operate pumps in mines its performance was expressed in simple practical terms. Boulton, writing to a client in 1776, stated:

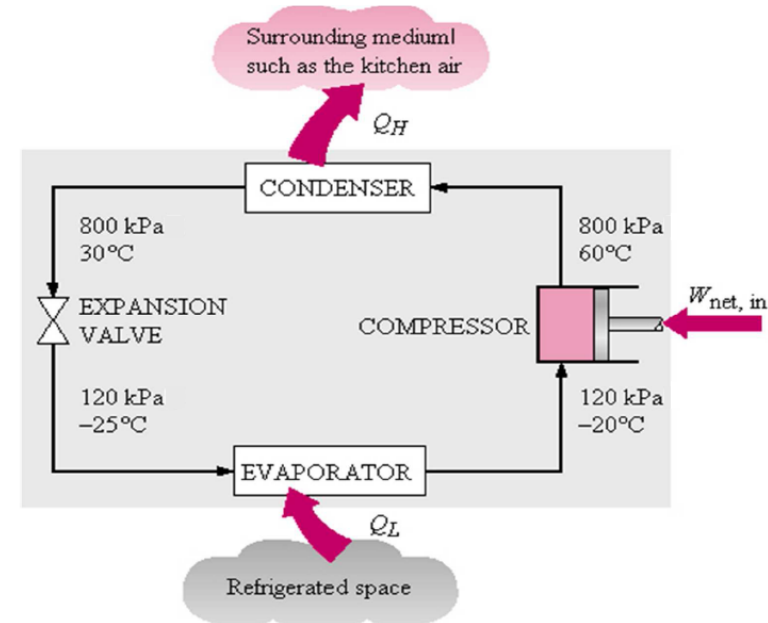
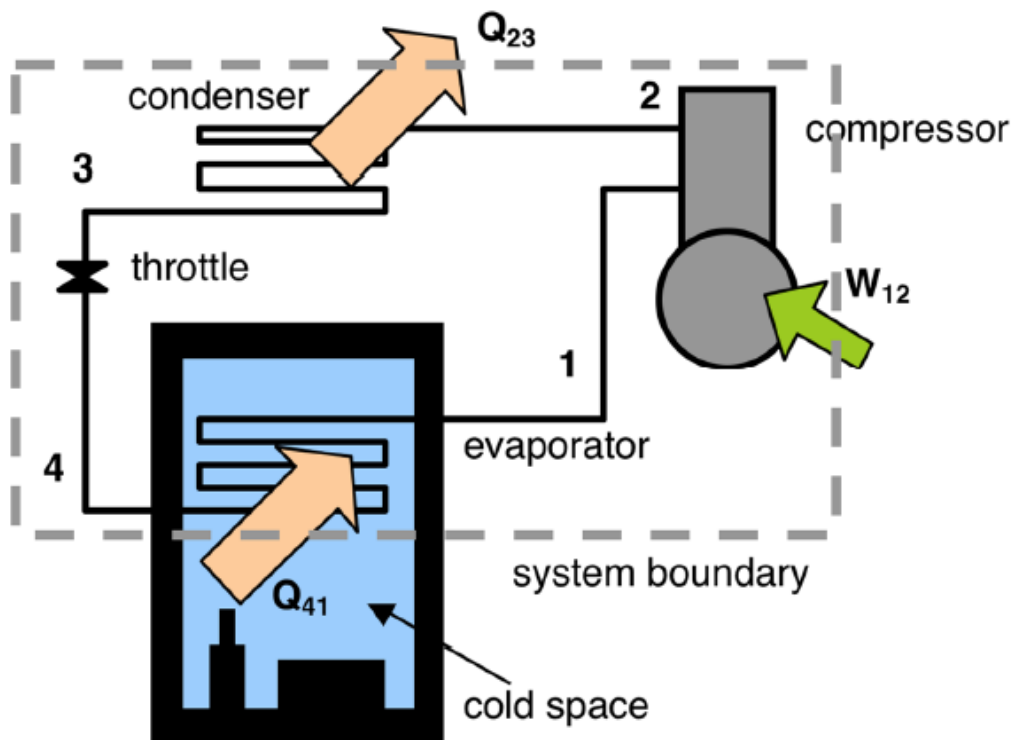
“We will guarantee that the engine shall raise 20,000 cubic feet of water 24 feet high with each hundredweight of coal burnt.”

The relationship between heat and work transfers was not understood at this time and it was not until the latter half of the 19th century that the First Law of Thermodynamics was stated clearly.

$$\eta_{\text{th}} = \frac{W_{\text{net}}}{Q_{\text{in}}}$$

Reversed heat engines

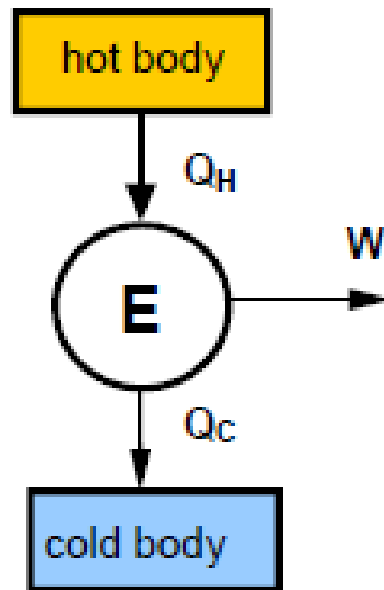
The heat engine may be run in reverse, for example, domestic and industrial refrigerators.



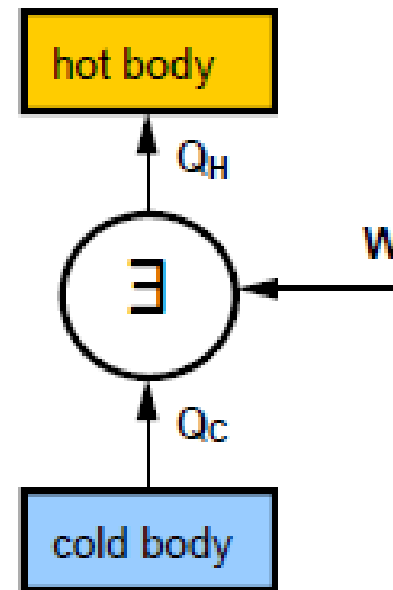
More details to be explained next chapter.

General heat engine and reversed heat engine

- Heat engines absorb heat from high temperature reservoir and generate mechanical work as output, in the meantime, reject heat to low temperature reservoir.
- Refrigerators absorb mechanical work and heat from low temperature reservoir, and reject heat to high temperature reservoir.



Normal Heat engine



Reversed heat engine

The second Law of Thermodynamics

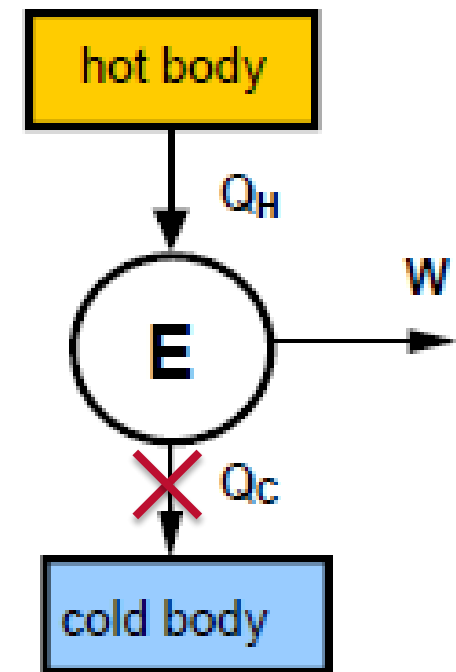
Thermal efficiency is defined as

$$\eta_t = \frac{W}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

If Q_C can be reduced (to zero), efficiency could increase (to 100%)!

This is known as a “Perpetual Motion Machine of the second kind” (PMM2)

It is proved that it's impossible to make such a machine!

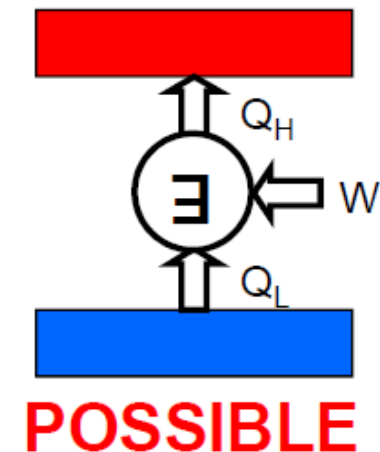
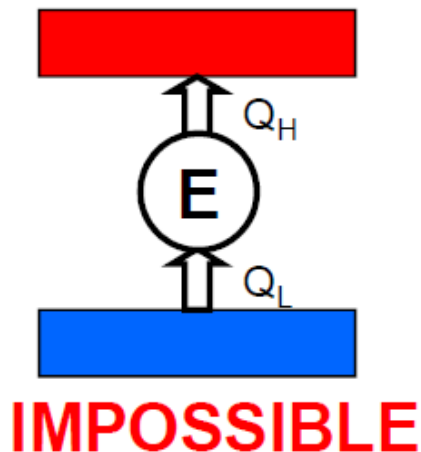


Normal Heat engine

The Second Law of Thermodynamics

Clausius Statement

The Clausius statement of the second law states that no device can transfer heat from a cooler body to a warmer one **without leaving an effect on the surroundings**.

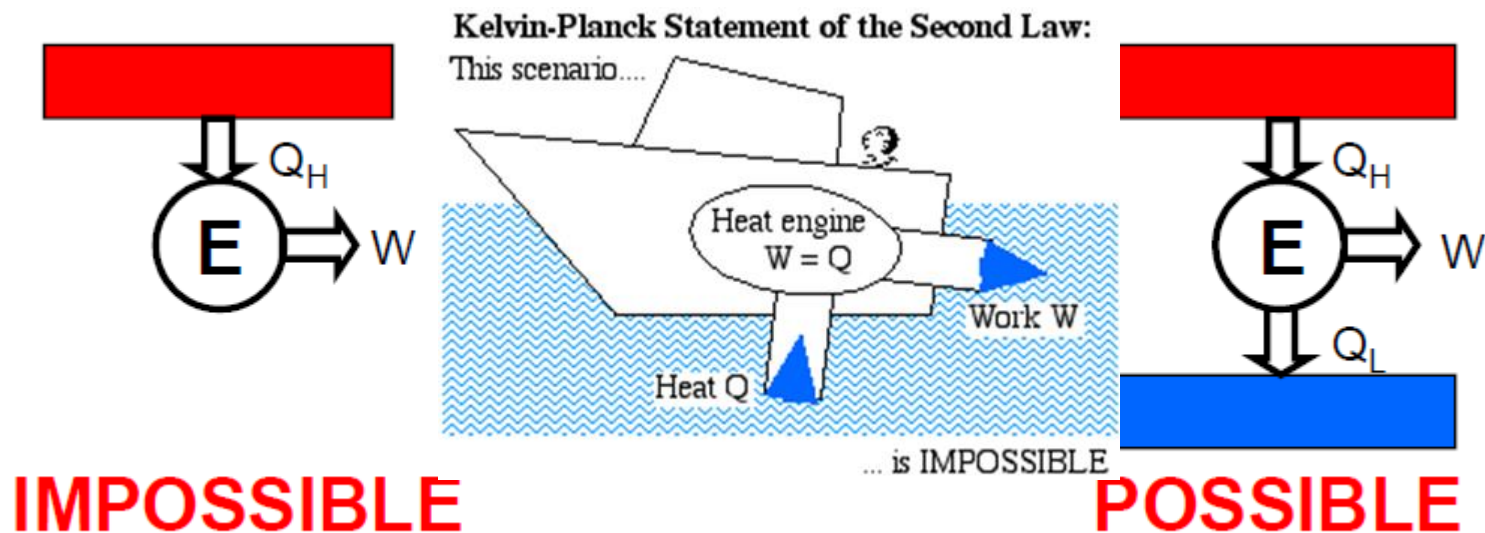


The Second Law of Thermodynamics

Kelvin-Planck Statement

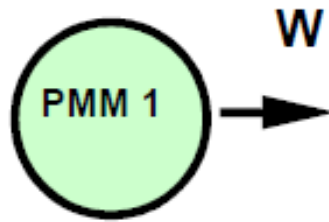
The Kelvin -Planck statement of the second law of thermodynamics states that no heat engine can produce a net amount of work while exchanging heat with a **single reservoir only**.

Any device that violates the first or the second law of thermodynamics is called a ***second type perpetual-motion machine***.

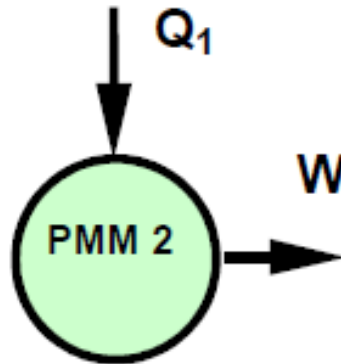


The Second Law of Thermodynamics

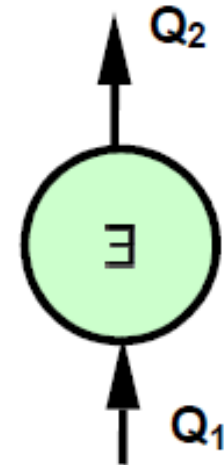
Summary of possible and impossible heat engines



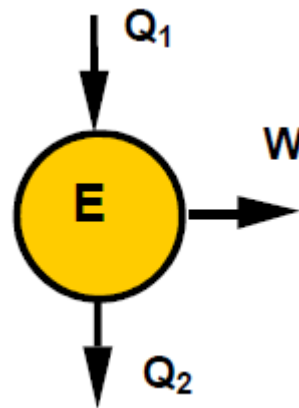
Impossible
(1st Law)



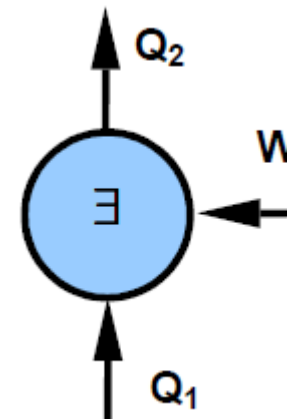
Impossible
(2nd Law KP statement)



Impossible
(2nd Law Clausius statement)

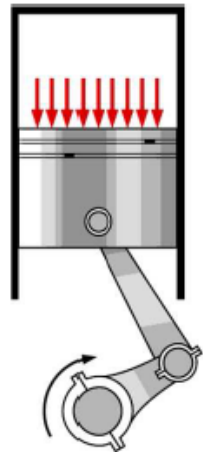
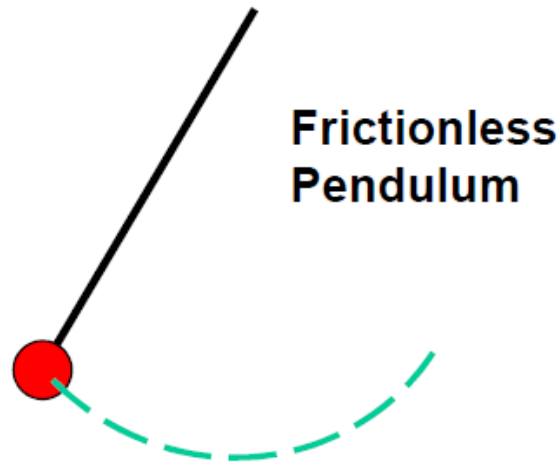


Possible
(Heat engine)

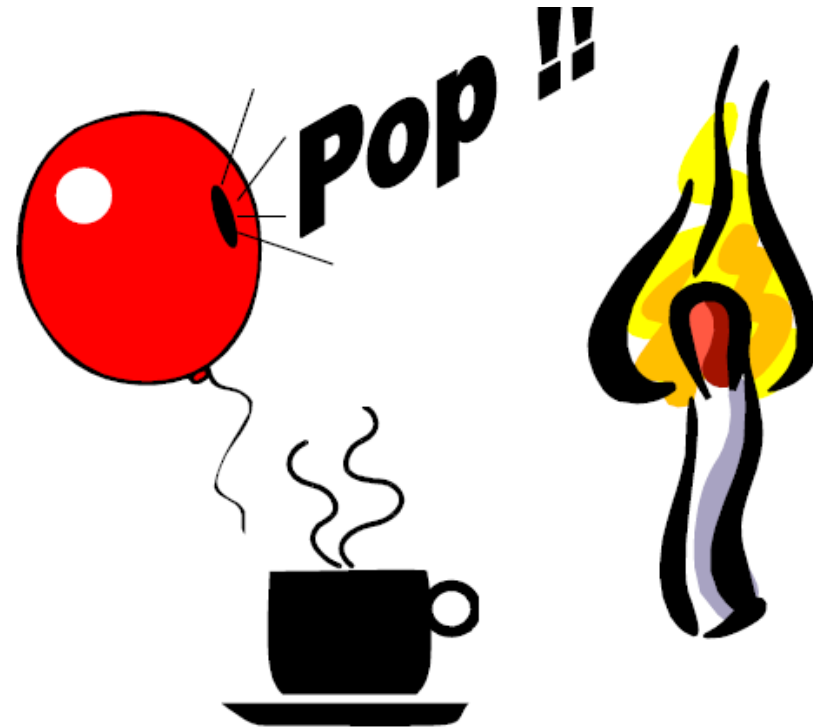


Possible
(reversed heat engine)

Reversible and Irreversible processes



Quasi-
equilibrium
expansion
and
compression
of a gas



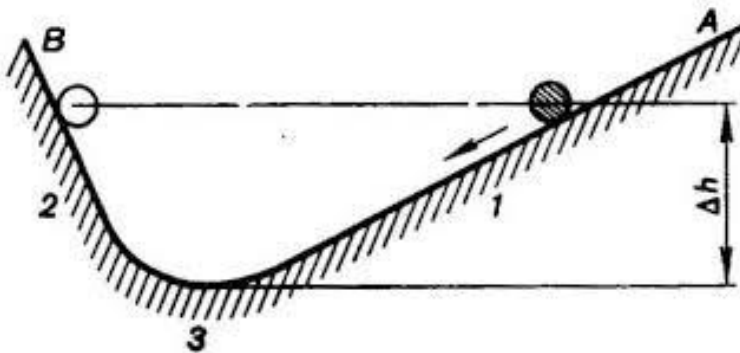
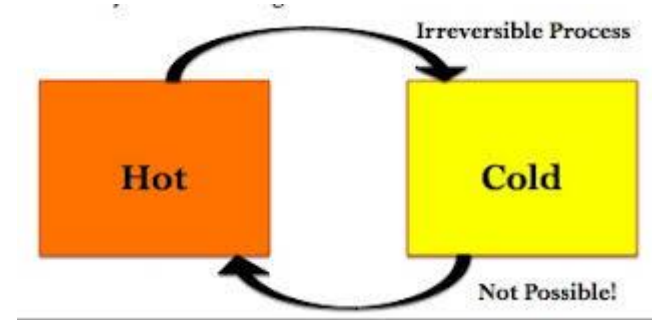
Reversible Process:

A process which can be reversed without leaving any trace on the surroundings

Reversible and irreversible processes

Causes of Irreversibility

- **Friction**
- **Heat transfer**
- **Non-quasi-equilibrium processes**
i.e. rapid compression/expansion
- **Mixing**

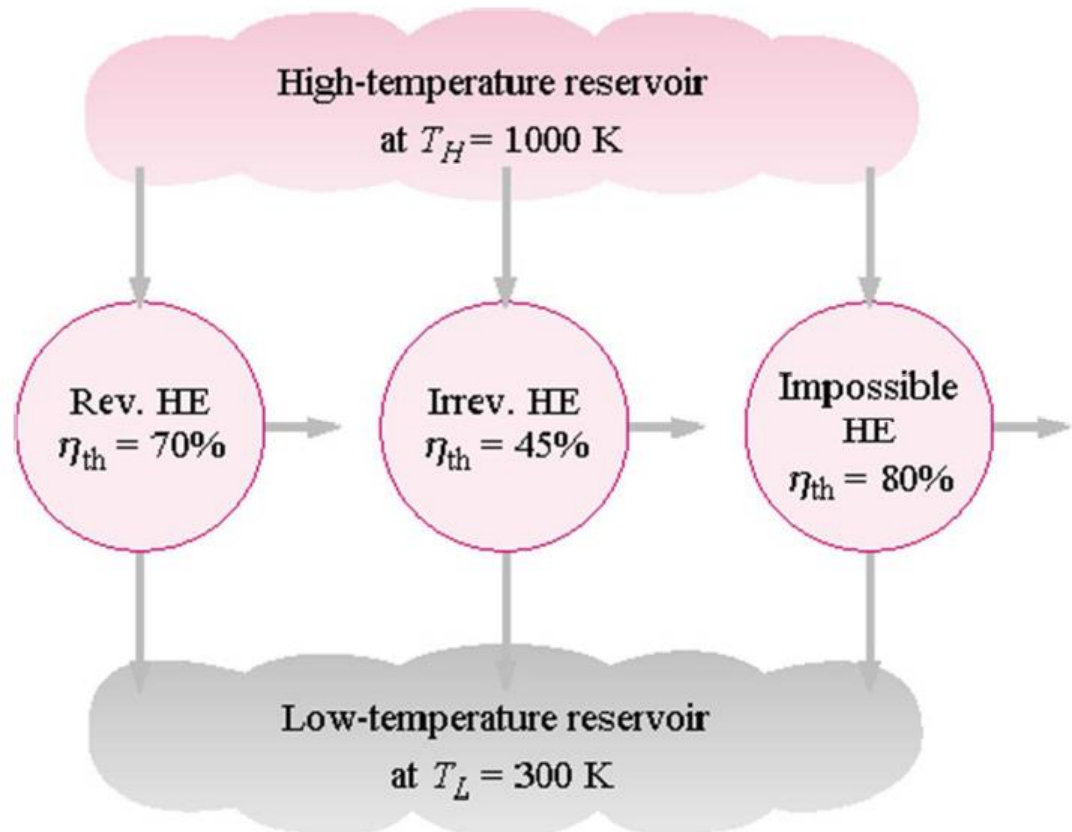


Reversible heat engine

Carnot principle

No heat engine can have a higher efficiency than a **Reversible heat engine** operating between the same high- and low- temperature reservoirs.

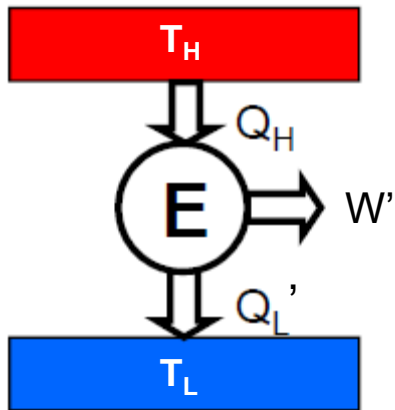
The efficiencies of all reversible heat engines operating between the same two reservoirs are the same.



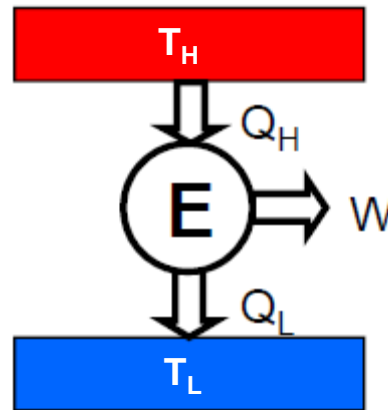
Prove of the Carnot principle

If there exists a hypothetical thermal engine that has higher efficiency than a reversible engine.

Operating in the same temperature reservoirs, assuming it has the same heat input Q_H , as it's more efficient, work output W' would be greater than W for the reversible engine, and Q_L' would be lower than Q_L .



Hypothetical engine



Reversible engine

$$W' > W$$

$$Q_L' < Q_L$$

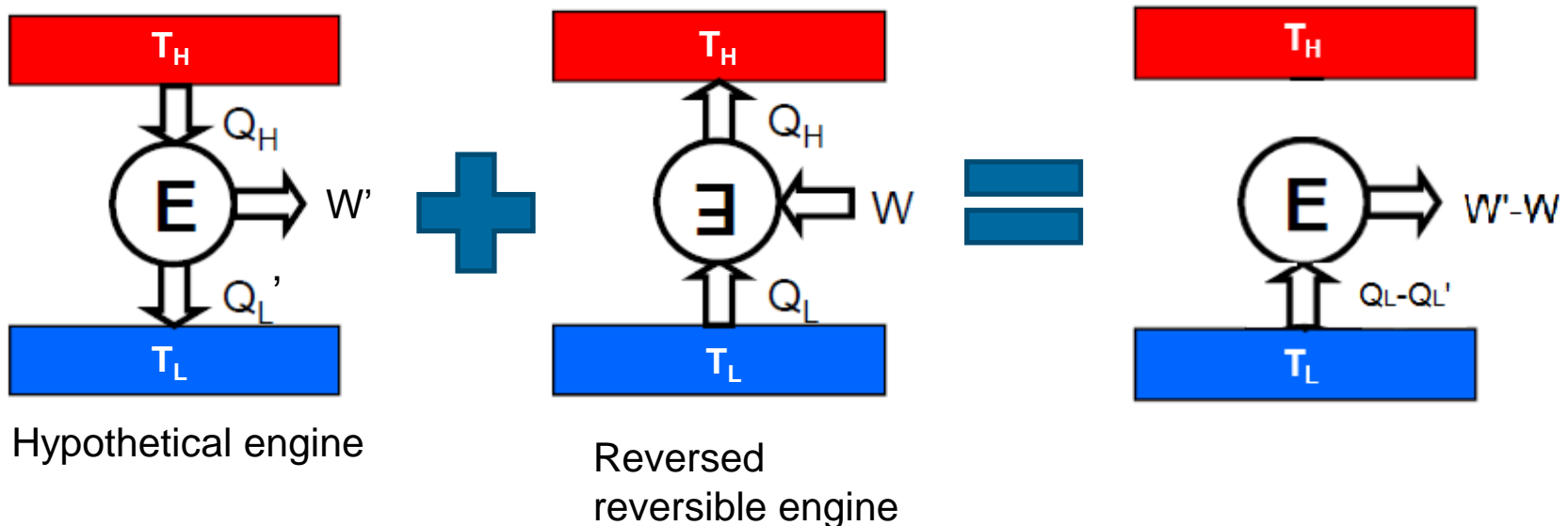
Prove of the Carnot principle

As the reversible engine is completely reversible, we can reverse all the process by just change the direct of the energy flow.

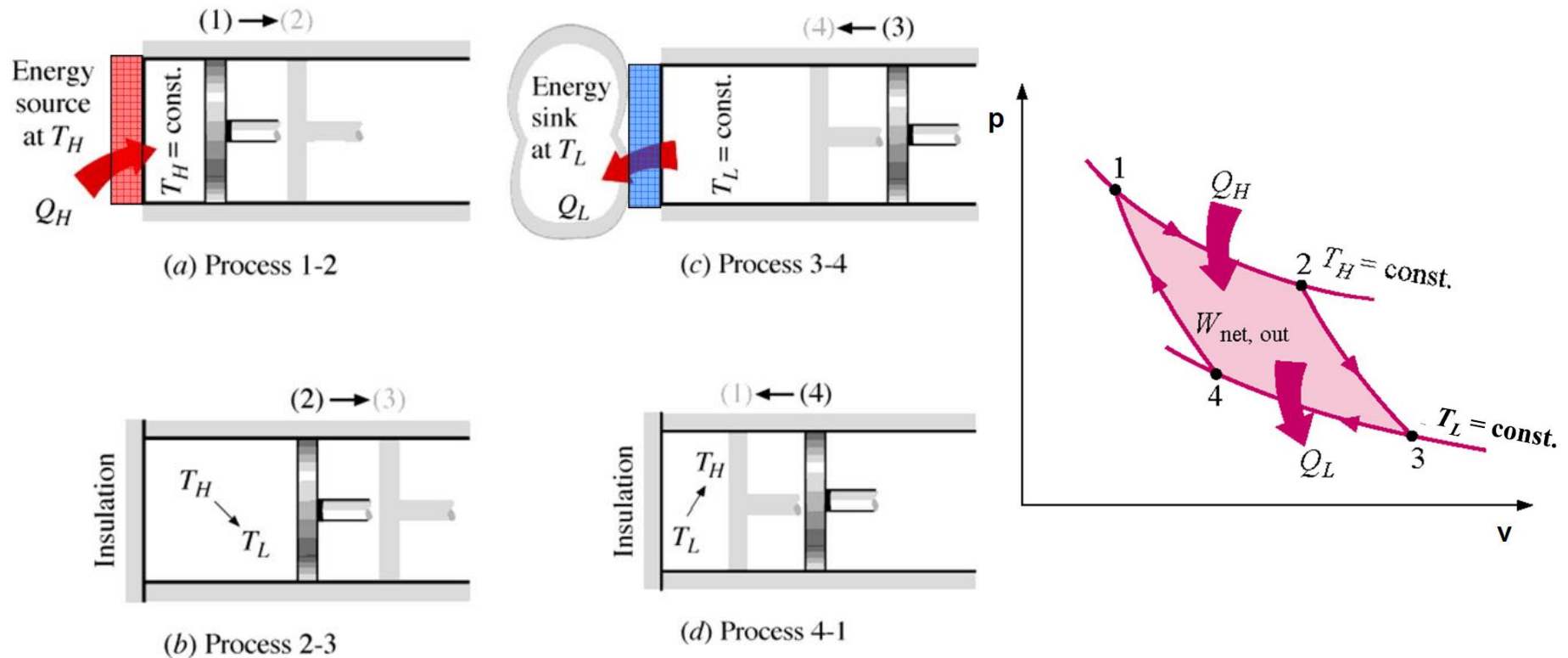
Combine these two engines together (consider as one big engine), we obtain a new engine. For the new engine, Q_H is cancelled out.

It absorbs heat from low temperature reservoir only, and output work.

From the second law, we know this is impossible. Therefore, it can be concluded that such an engine that has greater efficiency than a reversible engine is not possible.



Carnot cycle



- 1→2: isothermal heat addition (infinitesimally small temperature difference)
- 2→3: reversible adiabatic expansion
- 3→4: isothermal heat rejection (infinitesimally small temperature difference)
- 4→1: reversible adiabatic compression

NOTE: clockwise enclosed area, positive work (work output)

Thermodynamic temperature scale

A **thermodynamic temperature scale** is defined as a temperature scale that is independent of the properties of the substances that are used to measure temperature.

As all reversible heat engines have the same efficiency when operating between the same two reservoirs, the thermal efficiency is a function of the reservoir temperatures only.

i.e. $\eta_{th,rev} = f(T_H, T_L)$ or

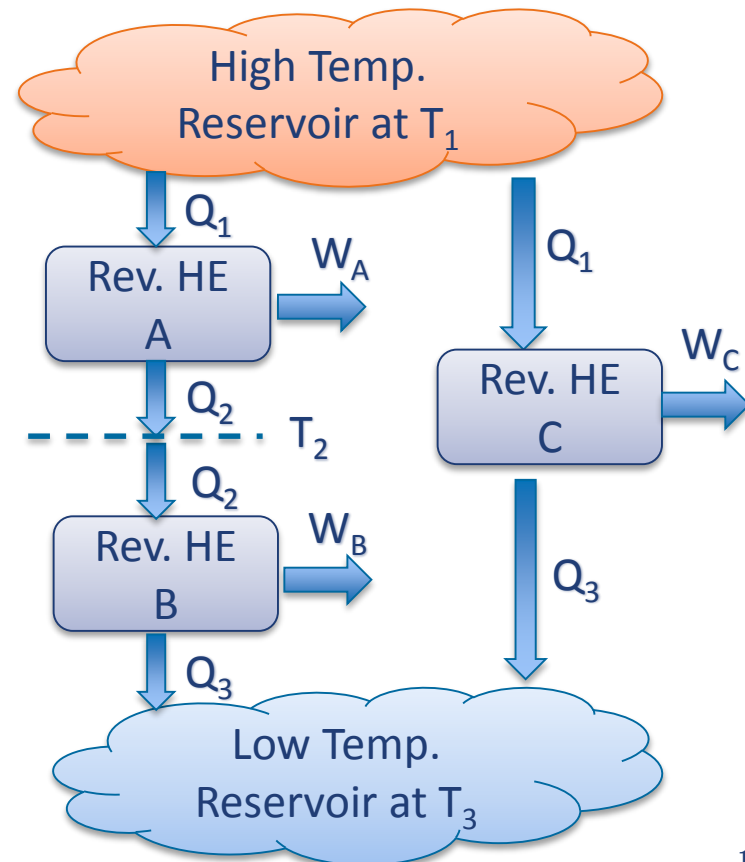
$$\frac{Q_H}{Q_L} = f'(T_H, T_L),$$

as $\eta_{th,rev} = 1 - \frac{Q_L}{Q_H}$

Consider the heat engines arrangement as shown on the right. As they are all reversible engines, based on Carnot principle:

If the heat addition is the same (Q_1), the heat rejection must be the same (Q_3), and

$$W_A + W_B = W_C$$



Thermodynamic temperature scale

For HE A, $\eta_A = \frac{Q_1 - Q_2}{Q_1}$, for HE B, $\eta_B = \frac{Q_2 - Q_3}{Q_2}$, and for HE C, $\eta_C = \frac{Q_1 - Q_3}{Q_1}$

From the previous slide, we can define a new function that:

$$\frac{Q_1}{Q_2} = f'(T_1, T_2)$$

Therefore: $\frac{Q_2}{Q_3} = f'(T_2, T_3)$, $\frac{Q_1}{Q_3} = f'(T_1, T_3)$

Because we have

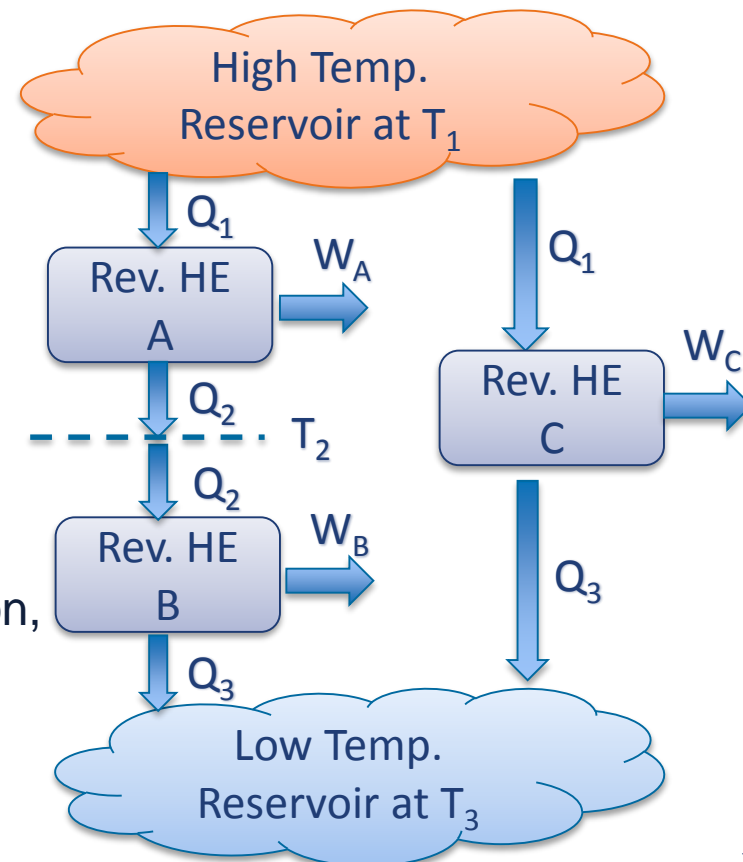
$$\frac{Q_1}{Q_3} = \frac{Q_1/Q_2}{Q_3/Q_2} = \frac{f'(T_1, T_2)}{f'(T_2, T_3)}$$

T_2 must cancel from the right hand side, also because T_2 is arbitrarily selected. This yields a new relationship

$$f'(T_1, T_2) = \frac{\Psi(T_1)}{\Psi(T_2)}$$

There are many relationship satisfies this equation, and the simplest is

$$\Psi(T) = T$$



Thermodynamic temperature scale

(continue...)

Thus we have

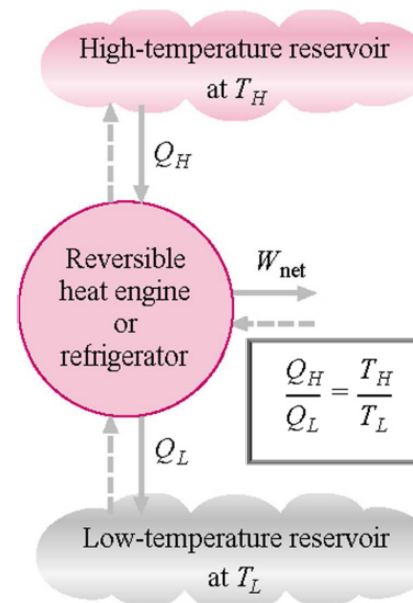
$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

And for efficiency $\eta_{12} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$

This is firstly defined by Kelvin, and this temperature scale is known as absolute temperature scale.

The triple point of water is defined as 273.16 K (0.01 °C), and water boiling point at 1 atm is defined as 373.15 K (100°C).

This definition is to be renewed this year which connects to Boltzmann constant.



For Reversible Cycles, the Temperature Ratio can replace the Heat Transfer Ratio

HENCE

$$\eta_R = \frac{T_H - T_L}{T_H}$$

OR

$$\eta_R = \frac{T_1 - T_2}{T_1}$$

Thermodynamic temperature scale

For ideal gases

Let's also consider the Carnot cycle running with an ideal gas.

For a closed system, $dw = p dv$,

For an ideal gas, $pv = RT$, therefore $dw = \frac{RT}{v} dv$

Also for an ideal gas, $du = c_v dT$

From 1st Law $dq = dw + du$

Substituting, $dq = \frac{RT}{v} dv + c_v dT$

For process 1→2

$$q_H = 0 + RT_H \ln \left(\frac{v_2}{v_1} \right)$$

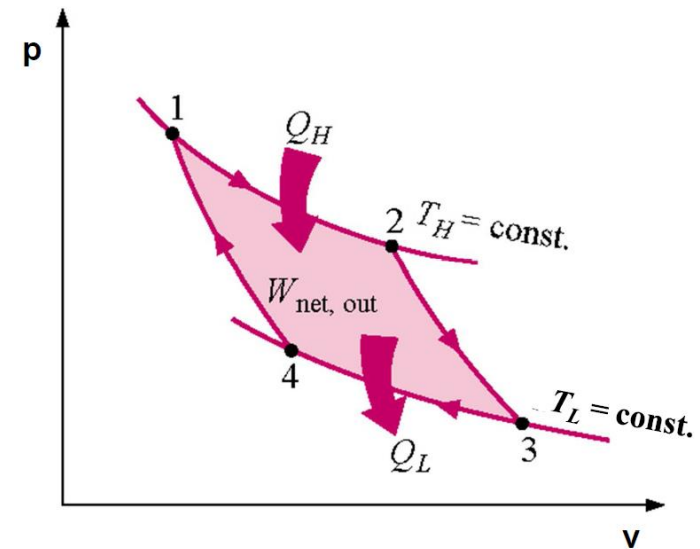
For process 3→4

$$q_L = 0 + RT_L \ln \left(\frac{v_3}{v_4} \right) \text{ (here consider } q_L \text{ as the magnitude of heat rejection)}$$

For the adiabatic processes 2→3 and 4→1,

$$2 \rightarrow 3: 0 = \int_{T_H}^{T_L} \frac{c_v}{T} dT + R \ln \frac{v_3}{v_2} \quad 4 \rightarrow 1: 0 = 0 = \int_{T_L}^{T_H} \frac{c_v}{T} dT + R \ln \frac{v_1}{v_4}$$

$$\text{Note: } \int_{T_H}^{T_L} \frac{c_v}{T} dT = - \int_{T_L}^{T_H} \frac{c_v}{T} dT, \text{ we have } R \ln \frac{v_3}{v_2} = -R \ln \frac{v_1}{v_4}$$



Thermodynamic temperature scale

For ideal gases

Continue...

$$R \ln \frac{v_3}{v_2} = -R \ln \frac{v_1}{v_4}$$

We have $\frac{v_3}{v_2} = \frac{v_4}{v_1}$

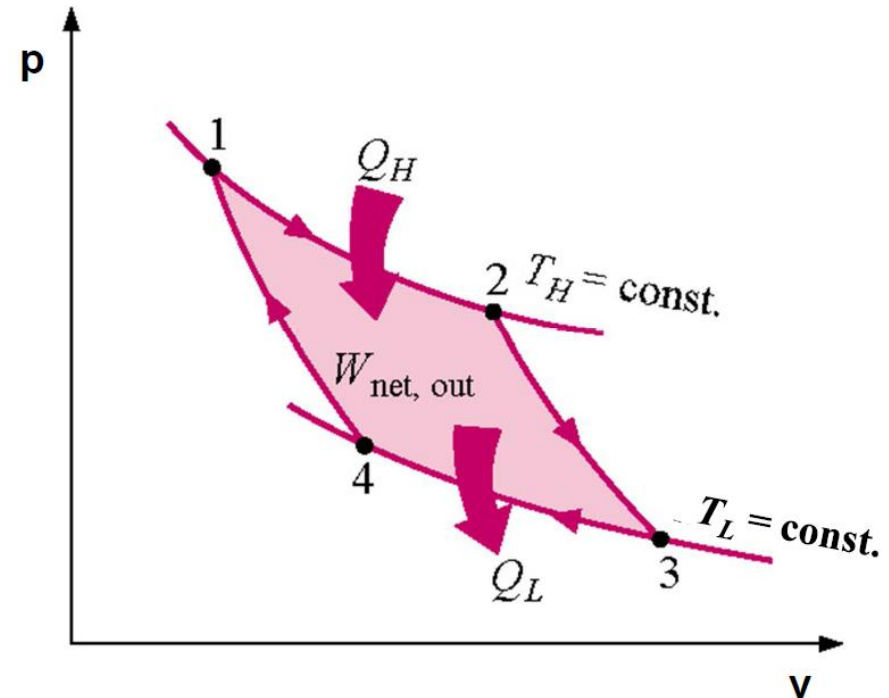
Or $\frac{v_2}{v_1} = \frac{v_3}{v_4}$

Therefore

$$\frac{q_L}{q_H} = \frac{RT_L \ln\left(\frac{v_3}{v_4}\right)}{RT_H \ln\left(\frac{v_2}{v_1}\right)} = \frac{T_L}{T_H}$$

And efficiency of Carnot cycle is

$$\eta_T = 1 - \frac{q_L}{q_H} = 1 - \frac{T_L}{T_H}$$



This is the same conclusion from previous derivation.

Reversible cycle thermal efficiency is solely determined by the high and low temperatures!

Reversible heat engine

$$\eta_T = 1 - \frac{Q_2}{Q_1} = 1 - T_2/T_1$$

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0$$

or

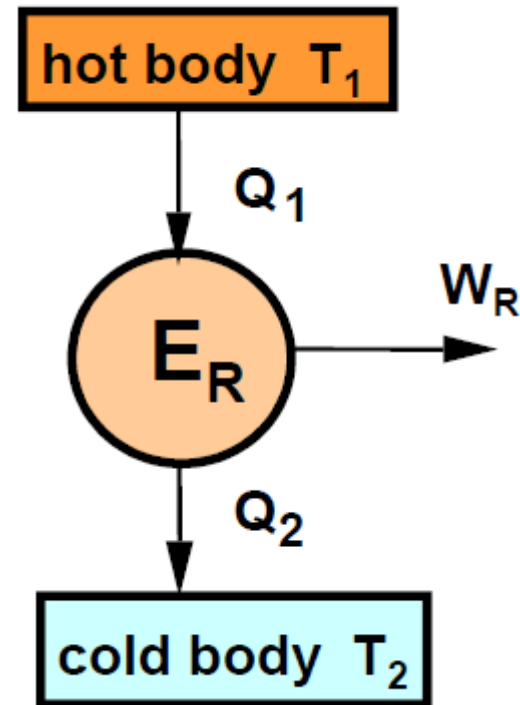
$$\oint \frac{dQ_R}{T} = 0$$

$$\int \frac{dQ_R}{T} = \text{property change} = S_1 - S_2$$

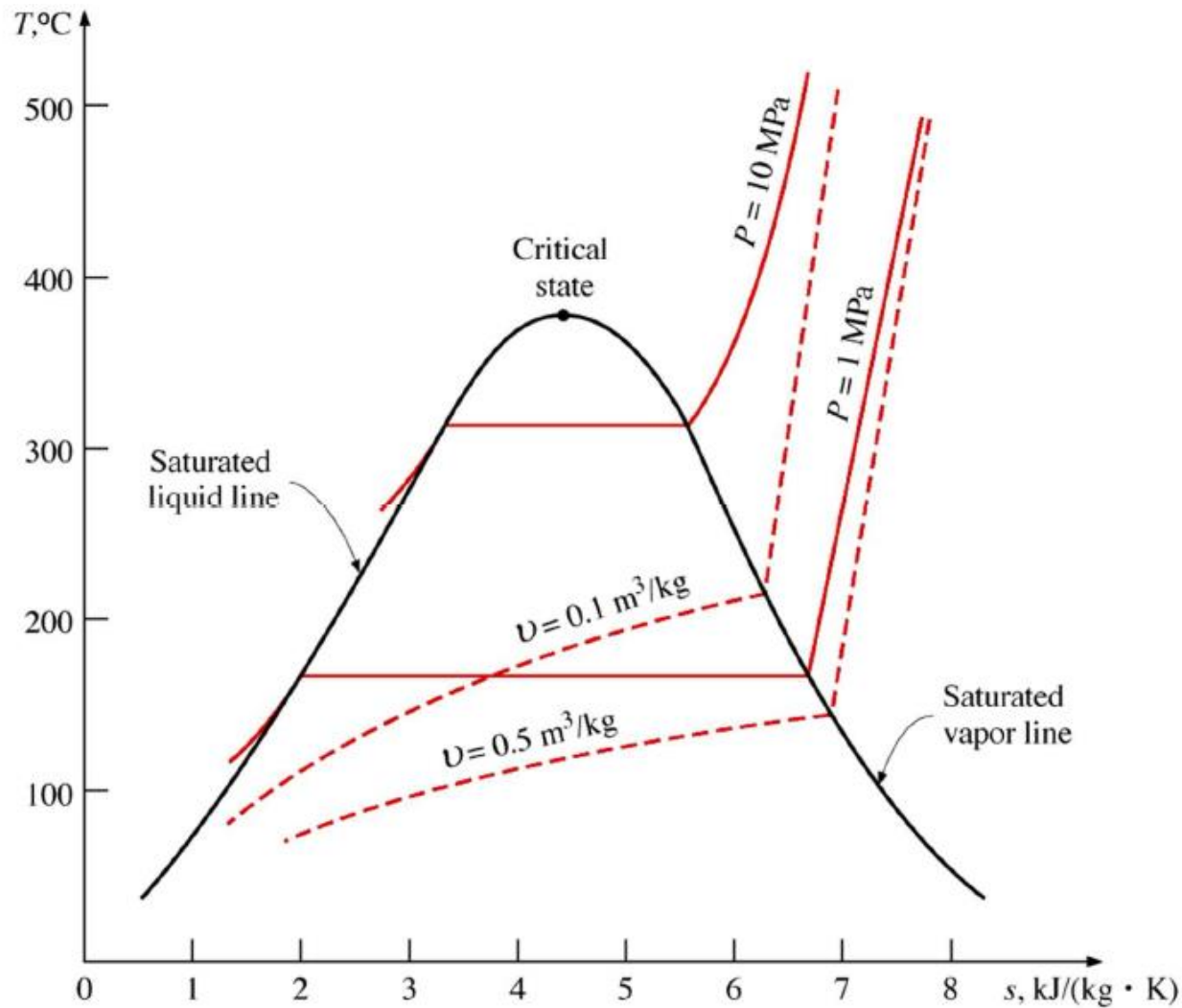
S=entropy (kJ/K)

Or $s=S/m$ =specific entropy (kJ/kg K)

NOTE: subscript R denotes for a reversible process.



T-s diagram for water



Entropy change and T-s diagram

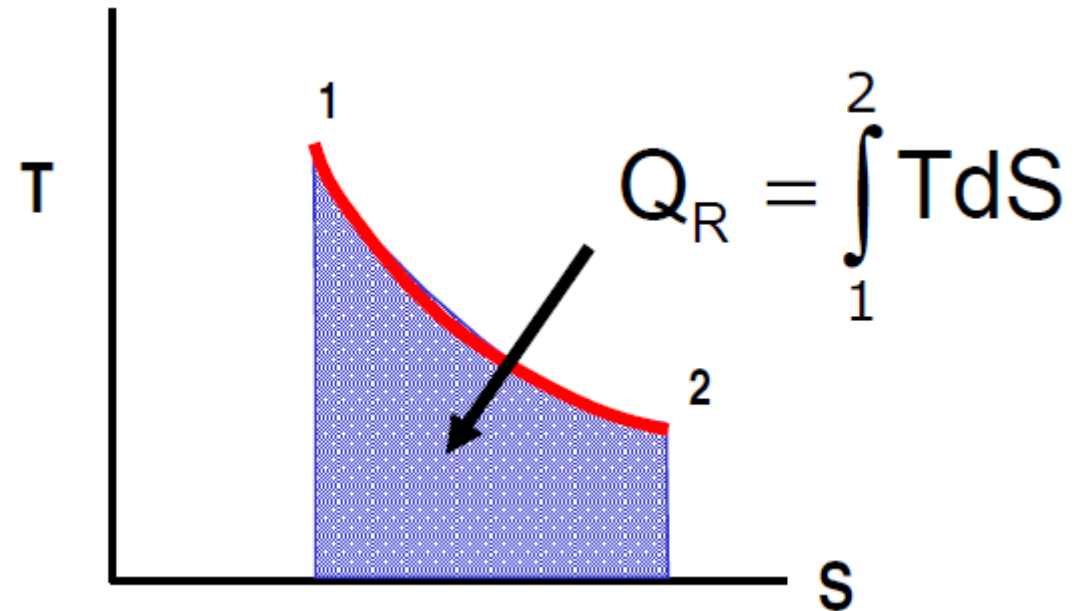
Chosen T-s diagram as

$$dq = Tds$$

Isentropic process

Entropy change = 0

$$\int \frac{dQ_R}{T} = 0$$

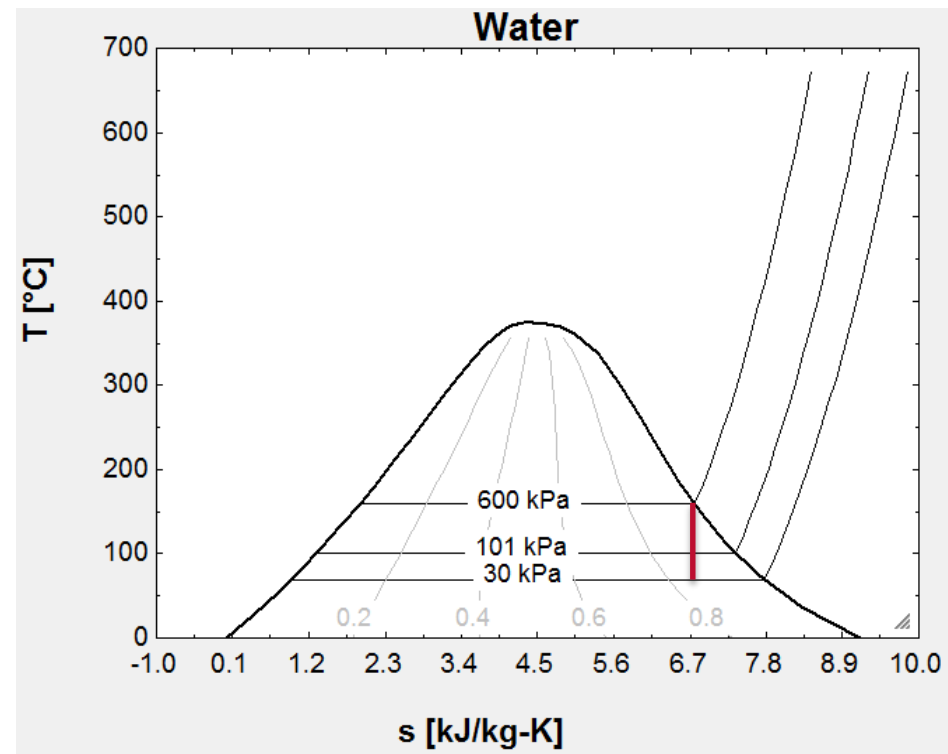
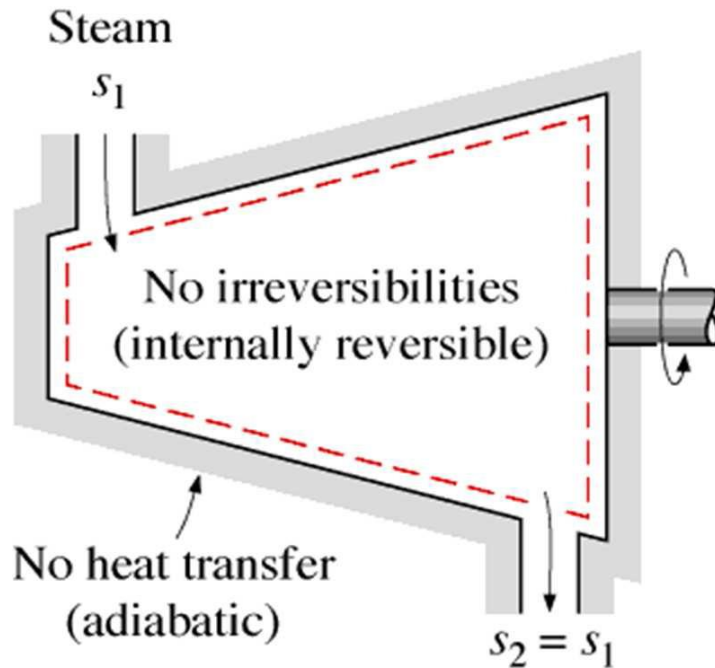


Isentropic = Adiabatic + Reversible

Note: If any 2 of these process descriptions is true then so is the 3rd.

Example

Dry saturated steam at 600 kPa flows steadily into a turbine which exhausts to a condenser at 30 kPa. Neglecting the kinetic energy of the steam at inlet and exit calculate the maximum possible specific work transfer from the turbine.



From steam table, saturated steam at 600kPa has the following properties:

$h_1=2757$ kJ/kg; $s_1=6.761$ kJ/kg K; $T_1=158.8$ °C

Expand to 30 kPa in an isentropic process,

Therefore $s_2=s_1=6.761$ kJ/kg K.

Using data at 0.3 bar, $s_f=0.944$, $s_g=7.767$,

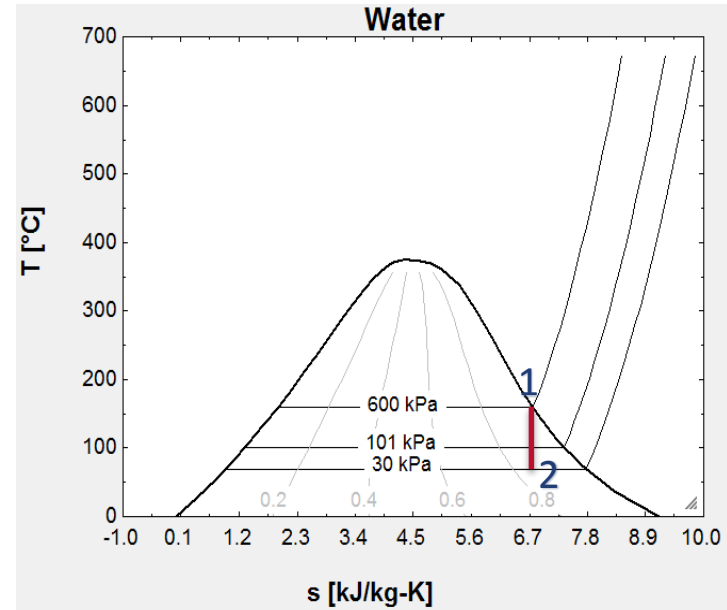
$$x = \frac{s_2 - s_f}{s_g - s_f} = 0.853$$

We can find enthalpy at 2:

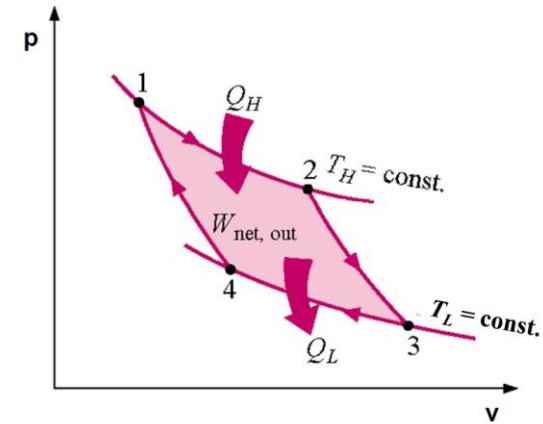
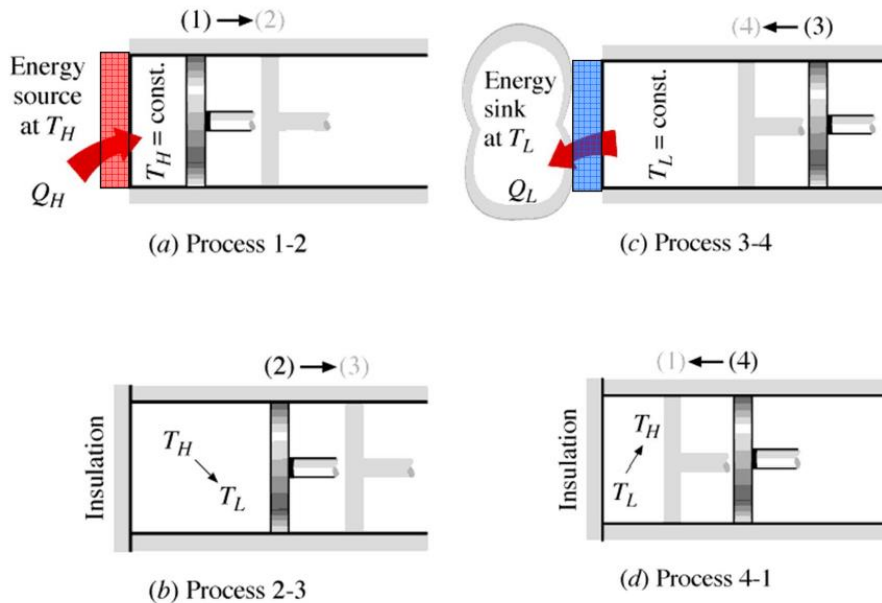
$$h_2 = h_f(1 - x) + h_g x = 289(1 - 0.853) + 2625 \times 0.853 = 2280.6 \text{ kJ/kg}$$

The maximum possible specific work transfer is the enthalpy change

$$w_{ext_max} = -(2280.6 - 2757) = 476.4 \text{ kJ/kg}$$

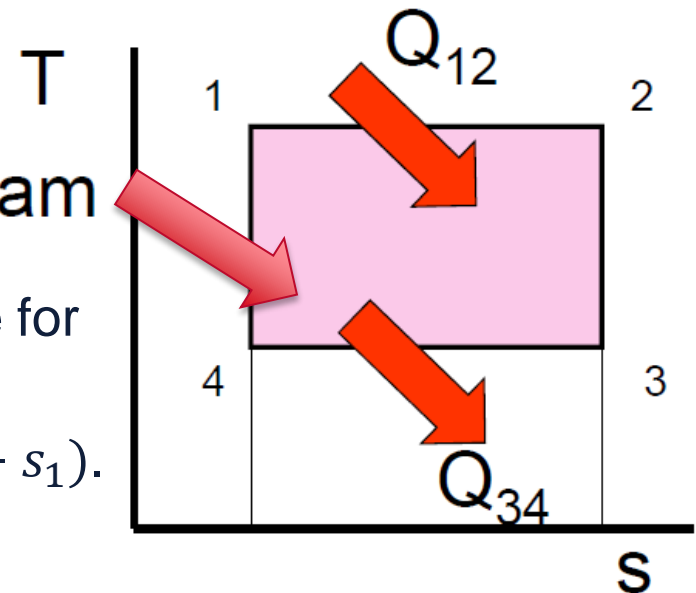


Revisit Carnot Cycle



$$W_{\text{net}} = \sum Q = \text{area of T-s diagram}$$

for a reversible engine, the entropy decrease for the hot reservoir equals the entropy increase for the cold reservoir ($s_3 - s_4 = s_2 - s_1$).



Principle of increase of entropy

Consider two heat engines between same heat reservoirs:
a reversible and an irreversible

$$\eta_R \geq \eta_I$$

For the reversible engine, we have

$$\eta_R = 1 - \frac{T_L}{T_H}$$

For the irreversible engine, we have

$$\eta_I = \frac{W}{Q_H}$$

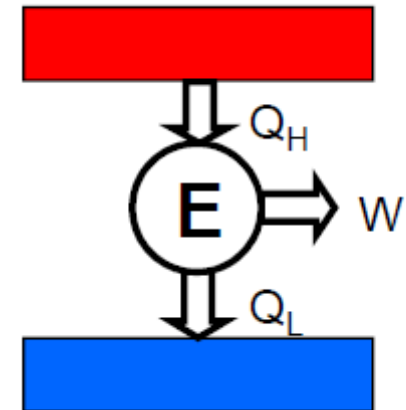
Therefore

$$\frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} \leq \frac{T_H - T_L}{T_H}$$

Rearrange

$$\frac{Q_H}{T_H} - \frac{Q_L}{T_L} \leq 0 \quad \text{or in general}$$

$$\oint \frac{dQ}{T} \leq 0$$



The definition of entropy is based on the Clausius inequality, given by

$$\oint \frac{dQ}{T} \leq 0 \quad (kJ / K)$$

where the equality holds for internally or totally reversible processes and the inequality for irreversible processes.

Note the previous equation we have is $\oint \frac{dQ_R}{T} = 0$
Mind the difference!

Consider a system that undergoes a cycle comprising an irreversible adiabatic process (1a2) and a reversible process (2b1)

For the **adiabatic** process (1a2)

$$\int_1^2 \left(\frac{dq}{T} \right)_a = 0$$

But irreversible

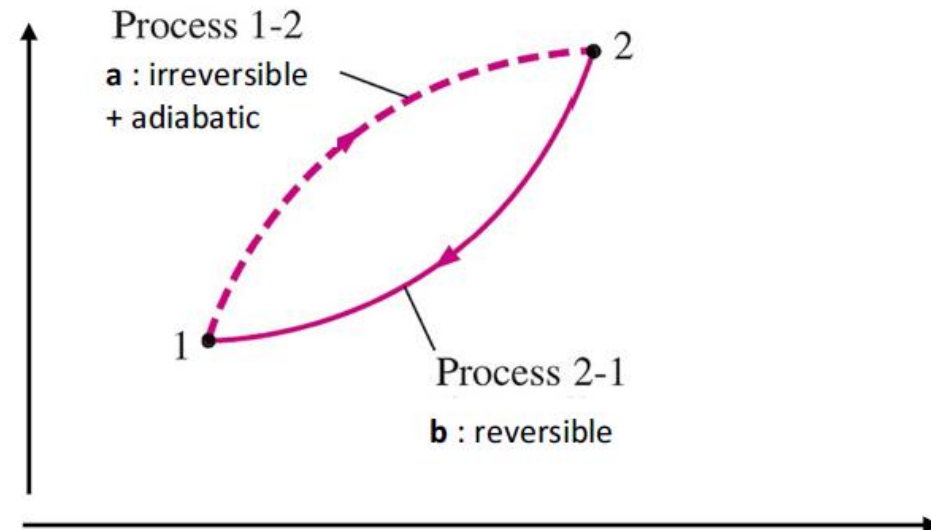
$$\int_1^2 \left(\frac{dq}{T} \right)_a \neq \int_1^2 ds$$

For the **reversible** process (2b1)

$$\int_2^1 \left(\frac{dq}{T} \right)_b = s_1 - s_2$$

Clausius inequality $\oint \frac{dQ}{T} \leq 0$

$$\text{Therefore} \quad \int_1^2 \left(\frac{dq}{T} \right)_a + \int_2^1 \left(\frac{dq}{T} \right)_b = 0 + (s_1 - s_2) \leq 0 \quad \Rightarrow \quad s_2 \geq s_1$$



Entropy generation

Entropy always increases!!!

The inequality part of the Clausius inequality combined with the definition of entropy yields an inequality known as the ***increase of entropy principle***, expressed as

$$S_{gen} \geq 0 \quad (kJ / K)$$

Where S_{gen} is the entropy generated during a process.

$$dS = \frac{dQ_R}{T} \quad \text{or} \quad dS = \frac{dQ}{T} + S_{gen}$$



Reversible process



Irreversible process

The previous conclusion leads to an important observation, namely that the entropy of an isolated system must either **increase** or **remain constant**.

In any process within an adiabatic boundary, whether expansion or compression, the entropy always increases due to the irreversibility inherent in any real process – only in an idealised reversible cycle does $S_2=S_1$

What is entropy

By definition, entropy is a working fluid **property** defined as

$$dS = \frac{dQ_R}{dT}$$

When heat transfer in/out across the system boundary, S can increase/decrease.

Reversible **work** does **not** change S.

By irreversibilities, S is generated, told by the Clausius inequality.

In an isolated system (where Q & W and mass flow = 0), S **increases** because the integral must be zero. Entropy is not a **conserved property** like energy or mass. S_{gen} is a measure of irreversibility and therefore how close any system comes to its reversible ideal.

Another very subtle corollary is that things only happen in one direction i.e. to increase entropy.

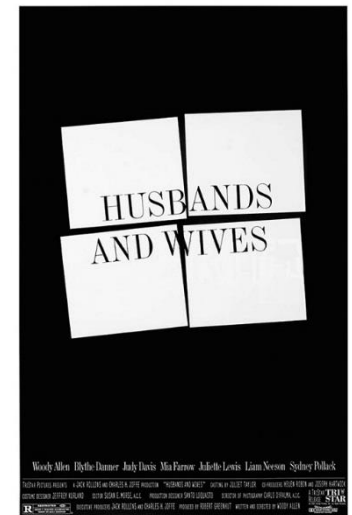
Entropy change is caused by **heat transfer** and **irreversibility**.

Heat transfer to a system increases the entropy, and heat transfer from a system decreases it.

The effect of **irreversibility** is always to increase the entropy.

“It’s the Second Law of Thermodynamics: Sooner or later everything turns to shit.”

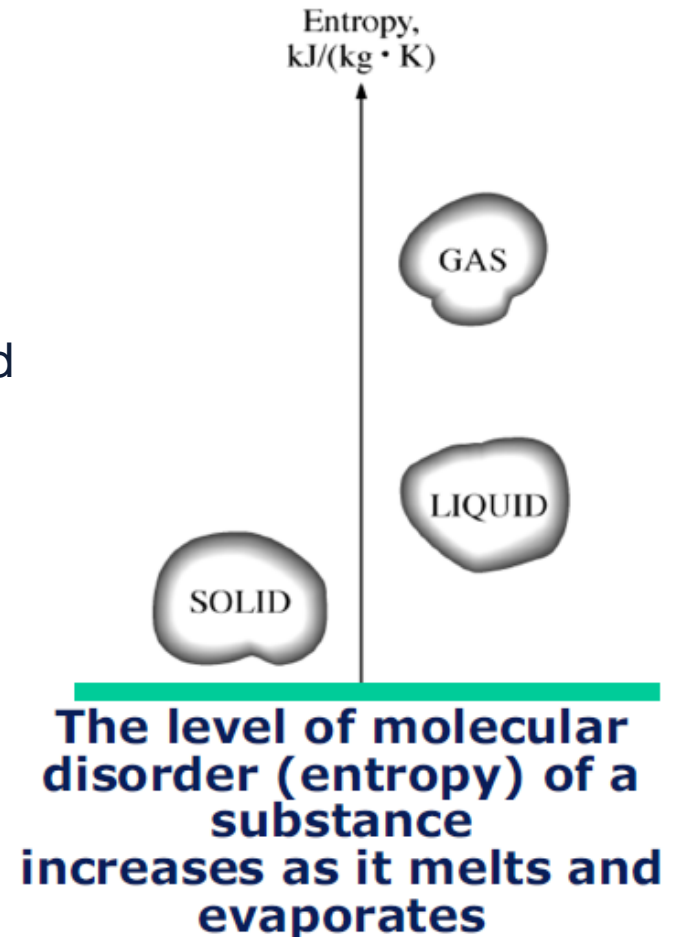
Woody Allen, in Husbands and Wives (1992).



What is entropy?

Entropy: a measure of **DISORDER**

- Entropy is minimum for solids, is higher for liquids, and higher still for gases and thus has come to be seen as a measure of disorder.
- Heat transfer only flows from hot to colder bodies (unless there is some work input) and in doing so entropy increases as the disorder in the colder body increases.
- Entropy is also linked to the **quality** of energy. This is to be discussed later.



T-ds relations

From the first law,

$$dq = dw + du$$

If the process is reversible, and $dw = pdv$, we have

$$dq_R = pdv + du$$

By definition, $\frac{dq_R}{T} = ds$, we have

$$Tds = du + pdv$$

Or if we use enthalpy, as $h = u + pv$, $dh = du + pdv + vdp$

$$Tds = dh - vdp$$

provide simple relationships for evaluating the entropy changes in any process.

T-ds relations for ideal gases and for liquids/solids

The entropy-change for a process involving an ideal gas can be summarized as follows:

$$s_2 - s_1 = c_V \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{v_2}{v_1} \right)$$

And

$$s_2 - s_1 = c_p \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{p_2}{p_1} \right)$$

For liquid or solid, as $v_2 \approx v_1$, and we don't distinguish c_p and c_v ,

$$s_2 - s_1 = c \ln \left(\frac{T_2}{T_1} \right)$$

Derivation of T-ds relations

$$\begin{aligned}h &= u + pv \\dh &= du + pdv + vdp \\ds &= \frac{dq_R}{T}\end{aligned}$$

First Law:

$$dq_R = du + pdv$$

Hence:

$$Tds = du + pdv = dh - vdp$$

For an ideal gas:

$$c_V = \frac{du}{dT} \qquad c_p = \frac{dh}{dT}$$

Therefore:

$$Tds = du + pdv = c_V dT + pdv$$

And

$$ds = c_V \frac{dT}{T} + p \frac{dv}{T} = c_V \frac{dT}{T} + \frac{R}{v} dv \quad (\text{with } pv = RT)$$

Hence:

$$\int_1^2 ds = c_V \int_1^2 \frac{dT}{T} + R \int_1^2 \frac{dv}{v}$$

Hence:

$$s_2 - s_1 = c_V \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{v_2}{v_1} \right)$$

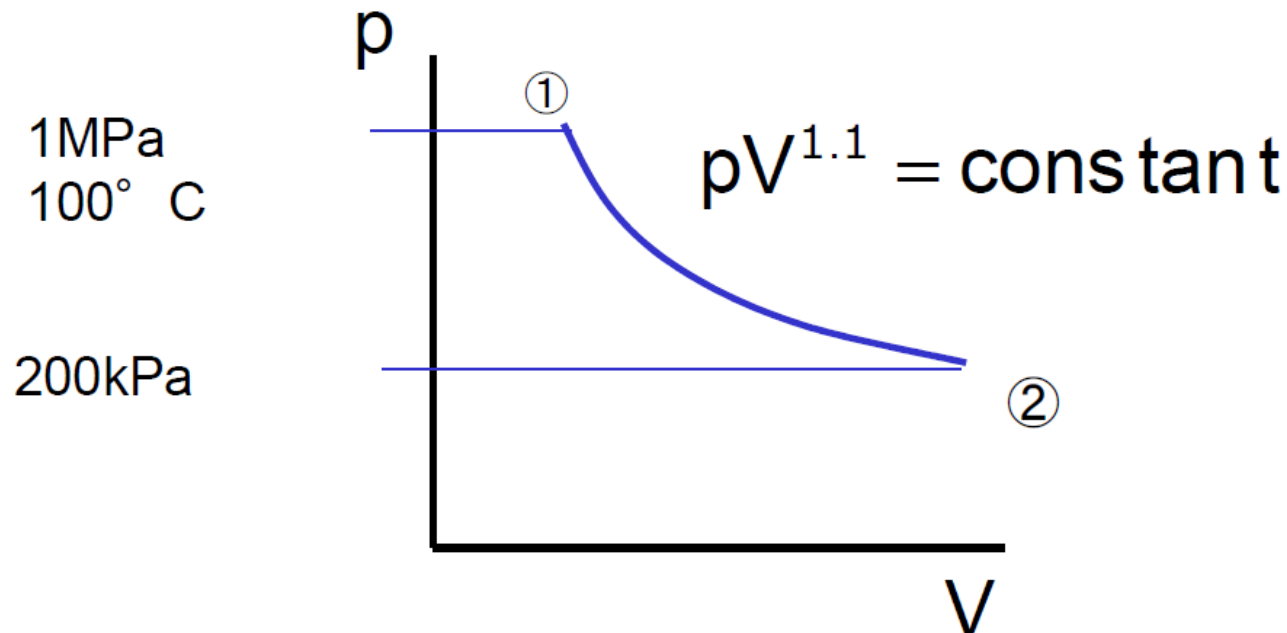
Try to derive:

$$s_2 - s_1 = c_p \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{p_2}{p_1} \right)$$

Example

- One kilogramme of air at 1MPa, 100°C expands to a pressure of 200kPa according to the relationship $pV^{1.1} = \text{constant}$

Calculate the change in entropy of the air.



@initial state 1

$$p_1 = 1 \text{ MPa}$$

$$T_1 = 373.15 \text{ K}$$

$$v_1 = \frac{RT_1}{p_1} = \frac{287 \times 373.15}{10^6} = 0.1071 \text{ m}^3/\text{kg}$$

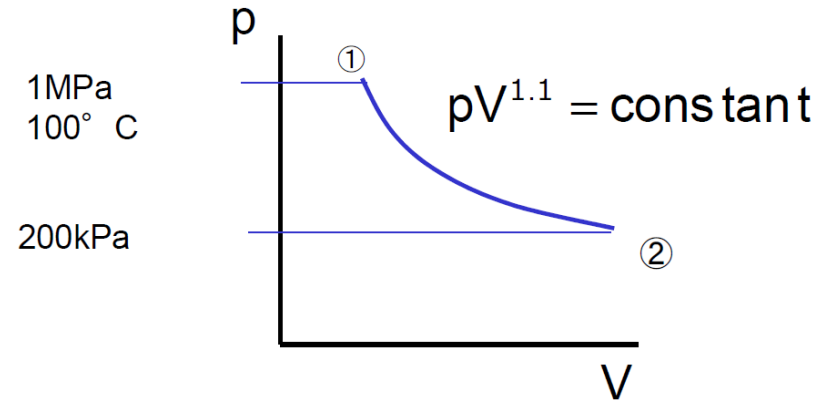
@final state 2

$$p_2 = 200 \text{ kPa}$$

$$p_1 v_1^{1.1} = p_2 v_2^{1.1} \Rightarrow v_2 = 0.463 \text{ m}^3/\text{kg}$$

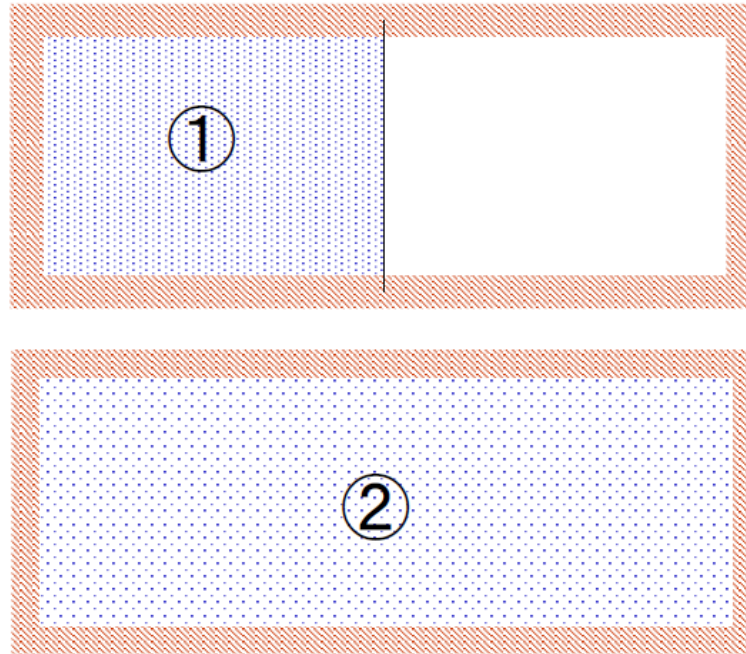
$$T_2 = \frac{p_2 v_2}{R} = 322.4 \text{ K}$$

$$\begin{aligned} s_2 - s_1 &= c_V \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{v_2}{v_1} \right) \\ &= 718 \ln \left(\frac{322.4}{373.15} \right) + 287 \ln \left(\frac{0.463}{0.1071} \right) \\ &= 315.2 \text{ J/kgK} \end{aligned}$$



Example

- One kilogramme of air at 600kPa, 300K expands into an evacuated insulated container so that its volume is doubled. Calculate the increase in entropy of the air.



Solution

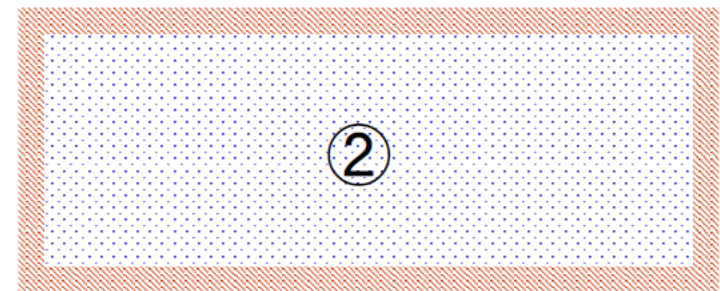
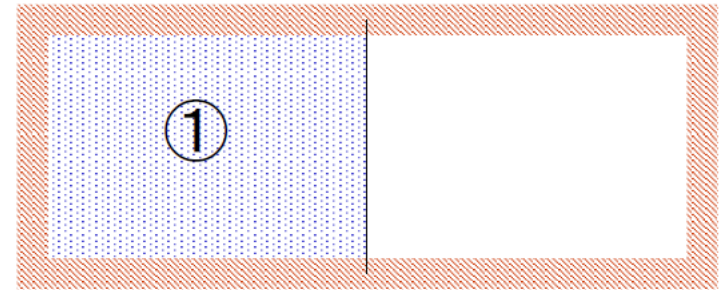
We use the equation $s_2 - s_1 = c_V \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{v_2}{v_1} \right)$

From 1-2, we have $q - w = \Delta u$

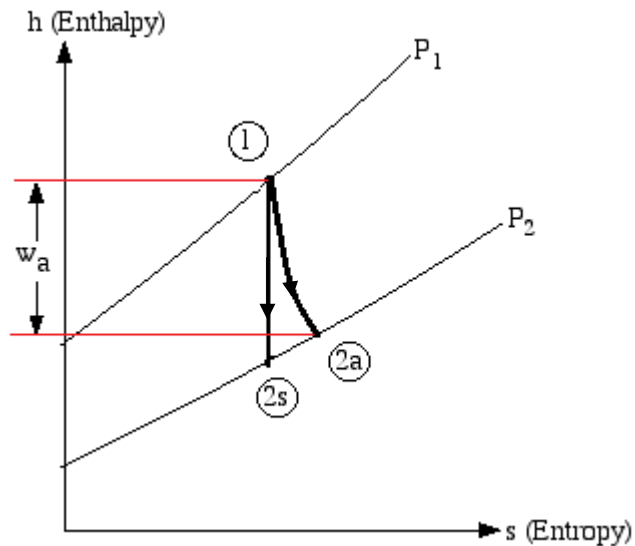
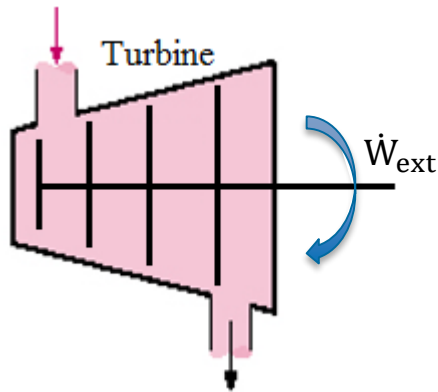
Where $q = 0$ (insulated) and $w = 0$ (evacuated)

Therefore $\Delta u = 0$, so $\Delta T = 0$

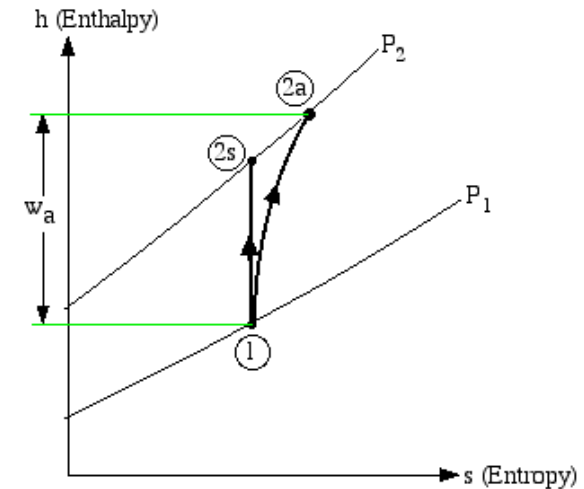
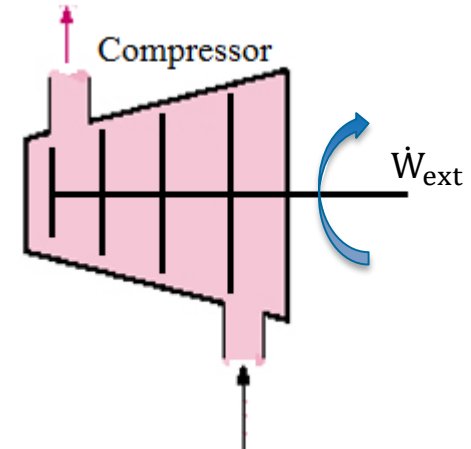
$$\begin{aligned} s_2 - s_1 &= c_V \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{v_2}{v_1} \right) = 0 + R \ln(2) \\ &= 287 \ln 2 = 198.9 \text{ J/kgK} \end{aligned}$$



Isentropic efficiency of turbine and compressor



$$\eta_T = \frac{\text{actual power output}}{\text{isentropic power output}} = \frac{h_1 - h_{2a}}{h_1 - h_{2s}}$$



$$\eta_C = \frac{\text{isentropic power input}}{\text{actual power input}} = \frac{h_{2s} - h_1}{h_{2a} - h_1}$$

The First Law of thermodynamics defines the *quantity* of energy.

The Second Law of thermodynamics deals with the *quality* of energy.

1 kWh of electricity and a certain amount of hot water contains 1 kWh of energy, they have the same amount of energy (quantity), but are they of the same value (quality)? (Energy quality of different forms)

1 kg of warm water at 50 °C, 1 bar (209.4 kJ) and 75 g of hot steam at 150 °C, 1 bar have the same energy (209.4 kJ). Can they convert to the same amount of work? (Energy quality of different grade)

We introduce a new concept of **Exergy**, which is the maximum useful work that could be obtained from the system at a given state in a specified environment.

Exergy is the maximum useful work that could be obtained from the system at a given state in a specified environment.

Given state in a specified environment

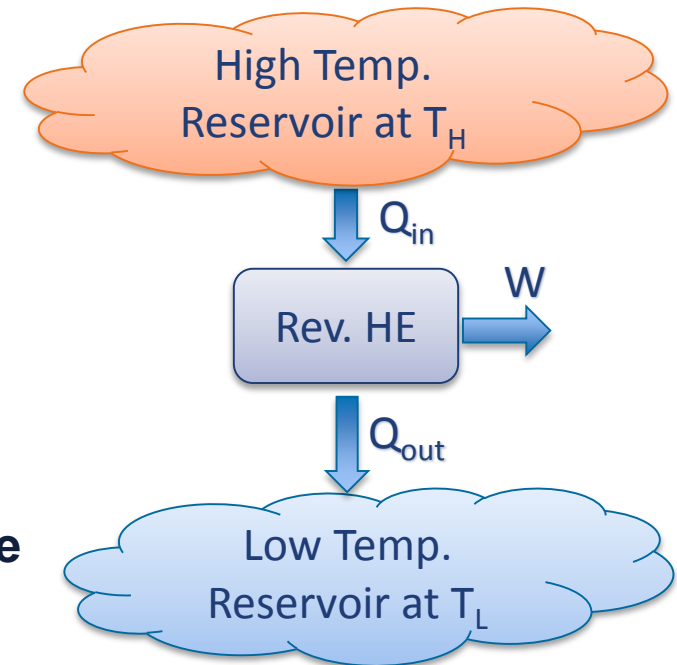
Not a variable, also known as

dead state

(As the Carnot efficiency is directly linked to low temperature reservoir conditions)

Maximum useful work

The work output is maximised when the process between the two states is executed in a **reversible manner**



Therefore, a system delivers the maximum possible work as it undergoes a *reversible process* from the *specified initial state* to the state of its environment, that is, the *dead state* (for example, by Carnot cycle). This represents the useful work potential of the system at the specified state and is called **exergy**.

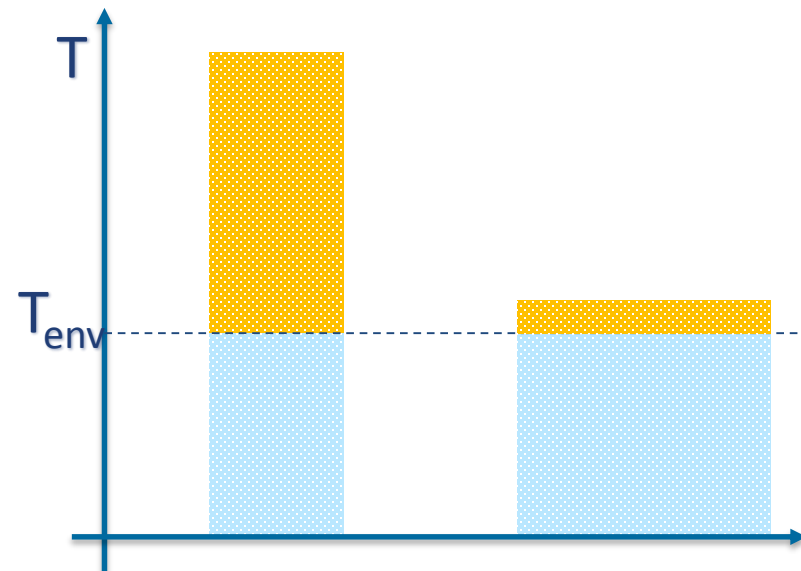
It represents the *upper limit* on the amount of work a device can deliver without violating any thermodynamic laws.

Previous question: electric energy vs. thermal energy, and thermal energy at different temperatures.

Electric/mechanical energy: pure exergy (100%)

Thermal energy: capped by the second law, higher temperature \rightarrow higher exergy

Ψ/ψ is used to represent exergy.



Exergy associated with P.E, K.E and E.E

Kinetic energy is a form of mechanical energy, therefore kinetic energy is pure exergy (can be converted to work entirely)

$$\psi_{ke} = ke = \frac{c^2}{2}$$

Potential energy is also a form of mechanical energy, therefore can be converted to work entirely as well.

$$\psi_{pe} = pe = gz$$

Electric energy can be 100% converted to mechanical energy (and vice versa), so electric energy is pure exergy as well

Example

Consider a large furnace that can transfer heat at a temperature of 1100 K at a steady rate of 3000 kW. Determine the rate of exergy flow associated with this heat transfer. Assume an environment temperature of 25°C.

The thermal efficiency of a reversible heat engine is

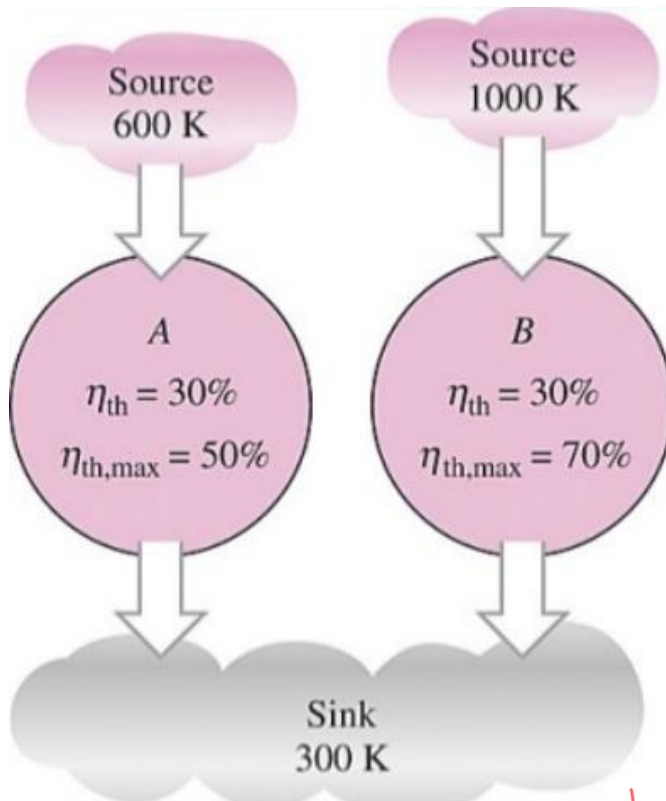
$$\eta_{t,max} = \eta_{t,rev} = 1 - \frac{T_L}{T_H} = 1 - \frac{298 \text{ K}}{1100 \text{ K}} = 72.9\%$$

The most energy can be converted to work is 72.9% of the heat received from the furnace. Thus the exergy is equivalent to the power produced by the reversible heat engine:

$$\dot{\Psi} = \eta_{t,rev} \dot{Q}_{in} = 0.729 \times 3000 = 2187 \text{ kW}$$

Second Law efficiency

Consider two heat engines have the same thermal efficiency.
Are they equally well designed?



Obviously, as B has a higher T_H , the HE B should deliver higher efficiency, as it has higher maximum efficiency (in a reversible manner).

Therefore the second law efficiency, a.k.a exergy efficiency, takes into consideration of the available exergy, i.e. the maximum possible performance

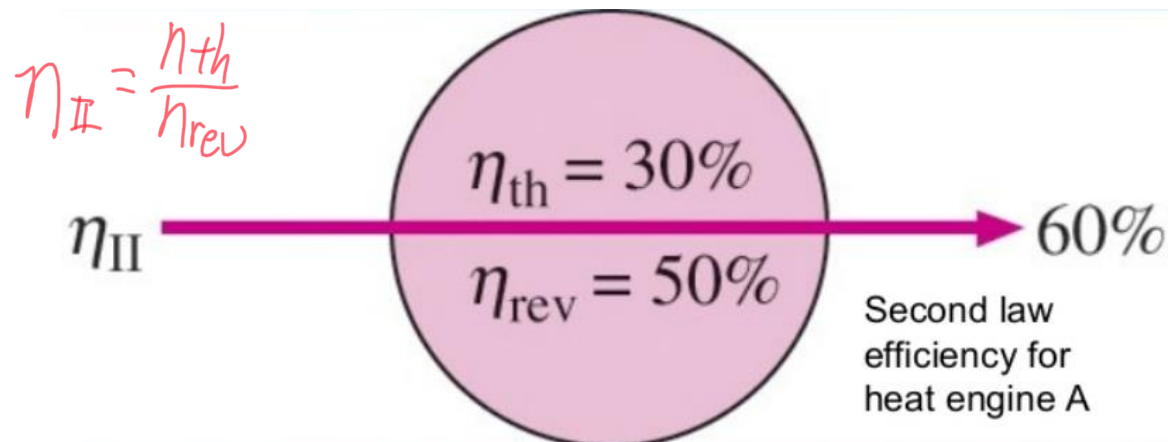
$$\eta = 1 - \frac{T_L}{T_H}$$

The second law efficiency is a measure of the performance of a device relative to what its maximum performance could be, which is under reversible conditions.

It provides a better view in comparison with the first law efficiency (thermal efficiency or energy efficiency) as not only it considers the quantity of heat source, also the quality.

What is the η_{II} of HE B?

What is the η_{II} of a reversible device?



Exergy of a closed system

For a reversible process, the system work

$$\delta W = p dV = (p - p_0) dV + p_0 dV = \delta W_{b,useful} + p_0 dV$$

During this process, heat transferred from the system and assume there exists a heat engine to utilise the heat. The work can be produced by the heat engine is

$$\begin{aligned}\delta W_{HE} &= \left(1 - \frac{T_0}{T}\right) \delta Q = \delta Q - \frac{T_0}{T} \delta Q \\ &= \delta Q - \left(T_0 \frac{\delta Q}{T}\right) = \delta Q - (-T_0 dS)\end{aligned}$$

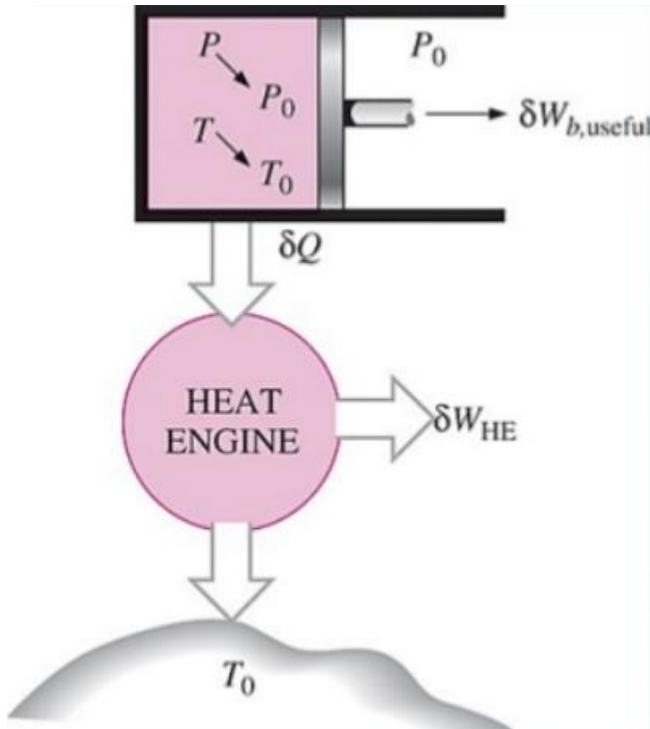
Or $\delta Q = \delta W_{HE} - T_0 dS$

And the first law

$$-\delta Q - \delta W = dU \quad (\text{taking the direction of } Q \text{ as from the system})$$

Substitute and integrate (from initial to dead state):

$$\begin{aligned}W_{total\ useful} &= W_{HE} + W_{b,useful} \\ &= (U - U_0) + p_0(V - V_0) - T_0(S - S_0) \\ &= \Psi\end{aligned}$$



Exergy change of a closed system

From last slide,

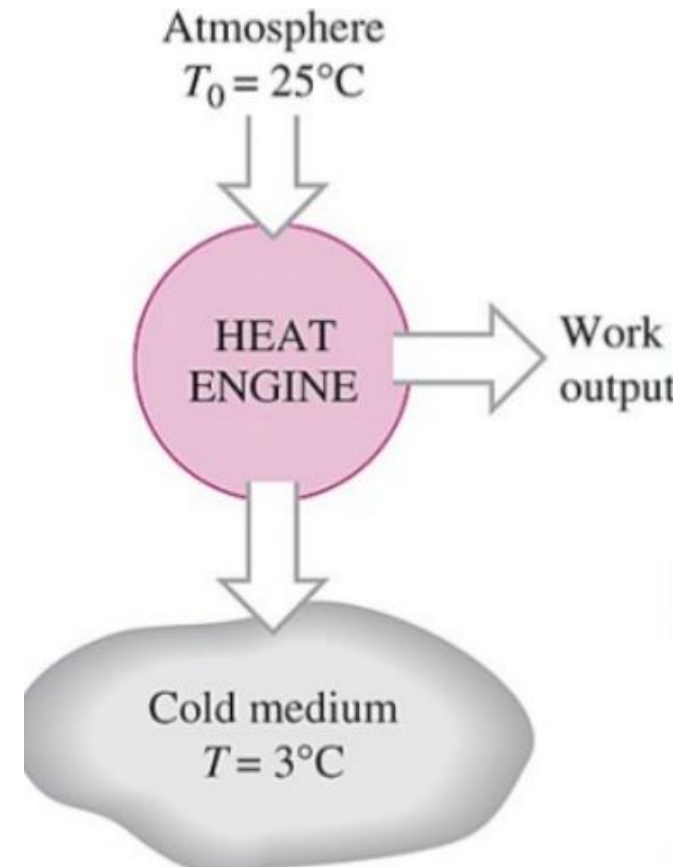
$$\Delta\Psi = (U_2 - U_1) + p_0(V_2 - V_1) - T_0(S_2 - S_1) + m(c_2^2 - c_1^2) + mg(z_2 - z_1)$$

Or in specific form:

$$\Delta\psi = (u_2 - u_1) + p_0(v_2 - v_1) - T_0(s_2 - s_1) + (c_2^2 - c_1^2) + g(z_2 - z_1)$$

The exergy change of a system is zero if the state of the system or the environment does not change, e.g. steady flow system

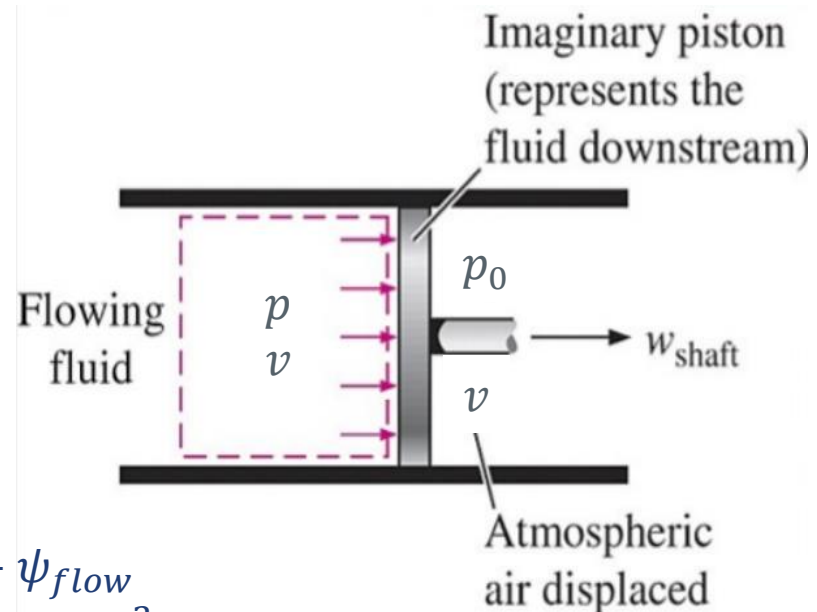
A closed system can only have positive or zero exergy. If the system has lower-than-environment temperature, it has the capability to deliver work.



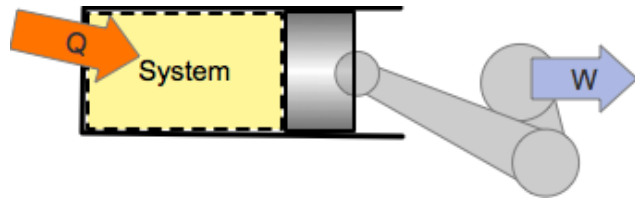
Exergy for open system

In open (flowing) systems, there is also flow energy.

The exergy of flow energy is the useful work that would be delivered by an imaginary piston in the flow v ($\psi_{flow} = pv - p_0v$)



$$\begin{aligned}
 \psi_{flowing\ fluid} &= \psi_{nonflowing\ fluid} + \psi_{flow} \\
 &= (u - u_0) + p_0(v - v_0) - T_0(s - s_0) + \frac{c^2}{2} + gz + pv - p_0v \\
 &= (u + pv) - (u_0 + p_0v_0) - T_0(s - s_0) + \frac{c^2}{2} + gz \\
 &= (h - h_0) - T_0(s - s_0) + \frac{c^2}{2} + gz
 \end{aligned}$$



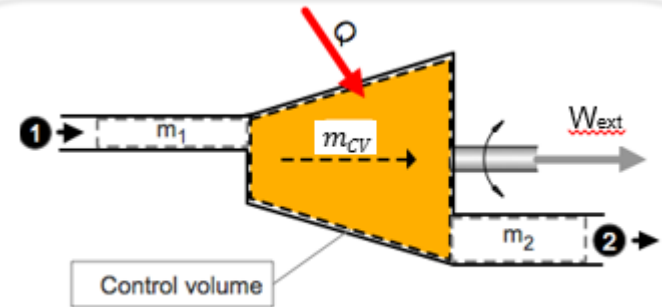
Closed system

Energy

$$e = u + \frac{1}{2}c^2 + gz$$

Exergy

$$\psi = (u - u_0) + p_0(v - v_0) - T_0(s - s_0) + \frac{1}{2}c^2 + gz$$



Open system

Energy

$$e = h + \frac{1}{2}c^2 + gz$$

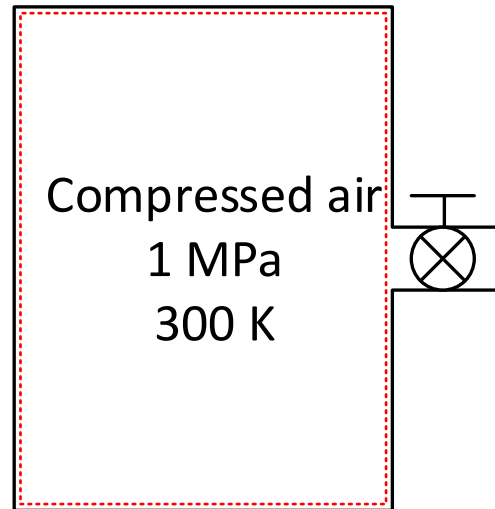
Exergy

$$\psi = (h - h_0) - T_0(s - s_0) + \frac{1}{2}c^2 + gz$$

Example

A 200 m³ rigid tank contains compressed air at 1 MPa and 300 K. Determine how much work can be obtained from this air if the environment conditions are 100 kPa and 300 K.

Assume ideal gas, k.e. and p.e. negligible, $R=287$ J/kgK



$$m = \frac{pV}{RT} = \frac{10^6(200)}{287(300)} = 2323 \times 10^3 g = 2323 kg$$

$$\begin{aligned} \Psi = m\psi &= m \left[(u - u_0)^{\wedge 0} + p_0(v - v_0) - T_0(s - s_0) + \left(\frac{c^2}{2} + gz \right)^{\wedge 0} \right] \\ &= m[p_0(v - v_0) - T_0(s - s_0)] \end{aligned}$$

We have $p_0(v - v_0) = p_0 \left(\frac{RT}{p} - \frac{RT_0}{p_0} \right) = RT_0 \left(\frac{p_0}{p} - 1 \right)$ (because $T=T_0$)

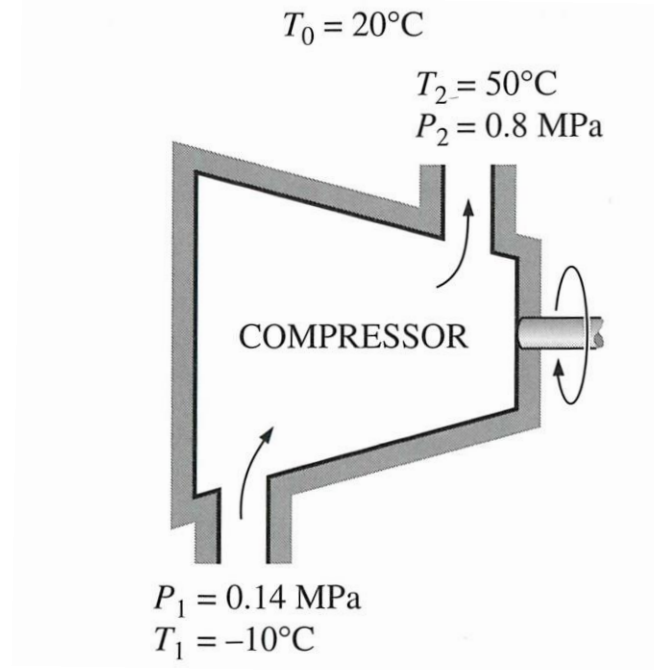
$$T_0(s - s_0) = T_0 \left(c_p \ln \frac{T}{T_0} - R \ln \frac{p}{p_0} \right) = -T_0 R \ln \frac{p}{p_0} \quad (\text{because } T=T_0)$$

Therefore

$$\begin{aligned} \psi &= RT_0 \left(\frac{p_0}{p} - 1 \right) + RT_0 \ln \frac{p}{p_0} = RT_0 \left(\frac{p_0}{p} - 1 + \ln \frac{p}{p_0} \right) \\ &= 287(300) \left(\frac{10^5}{10^6} - 1 + \ln \frac{10^6}{10^5} \right) = 120.76 \times 10^3 J/kg = 120.76 kJ/kg \\ \Psi &= 2323(120.76) = 281 MJ \end{aligned}$$

Example

Refrigerant R134a is to be compressed from 0.14 MPa and -10°C to 0.8 MPa and 50°C steadily by a compressor. Taking the environment conditions to be 20°C and 95 kPa. Determine the exergy change of the refrigerant during this process and the minimum work input that needs to be supplied to the compressor per unit mass of the refrigerant.



At inlet (from property table):

$$p_1 = 0.14 \text{ MPa}, T_1 = -10^\circ\text{C} \rightarrow h_1 = 246.36 \text{ kJ/kg}, s_1 = 0.9724 \text{ kJ/kgK}$$

At exit (from property table):

$$p_2 = 0.8 \text{ MPa}, T_2 = 50^\circ\text{C} \rightarrow h_2 = 286.69 \text{ kJ/kg}, s_2 = 0.9802 \text{ kJ/kgK}$$

The exergy change can be calculated as:

$$\begin{aligned}\Delta\psi &= \psi_2 - \psi_1 = (h_2 - h_1) - T_0(s_2 - s_1) + \Delta\text{k.e.}^{\nearrow 0} + \Delta\text{p.e.}^{\nearrow 0} \\ &= (h_2 - h_1) - T_0(s_2 - s_1) \\ &= (286.69 - 246.36) - 293(0.9802 - 0.9724) \\ &= 38.0 \text{ kJ/kg}\end{aligned}$$

and the minimum work needs to be supplied is the reversible work, which is the change of exergy

$$w_{in,min} = \Delta\psi = 38 \text{ kJ/kg}$$

- Heat engines, heat work and energy (understanding)
- Reversed heat engines (understanding)
- The 2nd Law of Thermodynamics (understanding)
- Reversibility and irreversibility (understanding)
- The Carnot engine and Carnot cycle (understanding)
- Thermodynamic temperature scale (understanding)
- Entropy, T-s diagram, increase of entropy and Clausius inequality (understanding & calculation)
- Entropy generation (understanding & calculation)
- Entropy change for ideal gases (understanding & calculation)
- Isentropic efficiency (understanding & calculation)
- Exergy and 2nd Law efficiency (understanding & calculation)