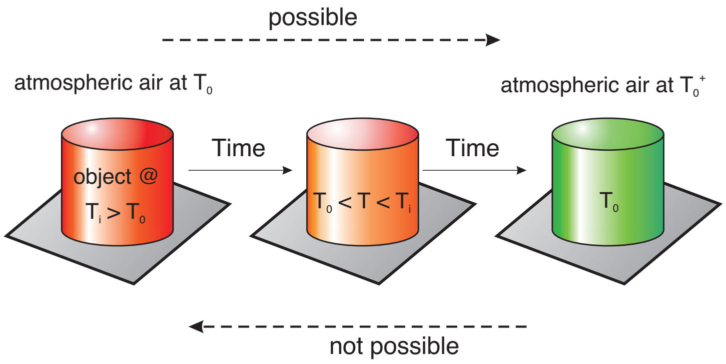
Entropy and the Second Law of Thermodynamics

Reading	**Problems**
7-1 → 7-3	7-88, 7-131, 7-135
7-6 → 7-10	8-24, 8-44, 8-46, 8-60, 8-73, 8-99, 8-128, 8-132,
8-1 → 8-10, 8-13	8-135, 8-148, 8-152, 8-166, 8-168, 8-189

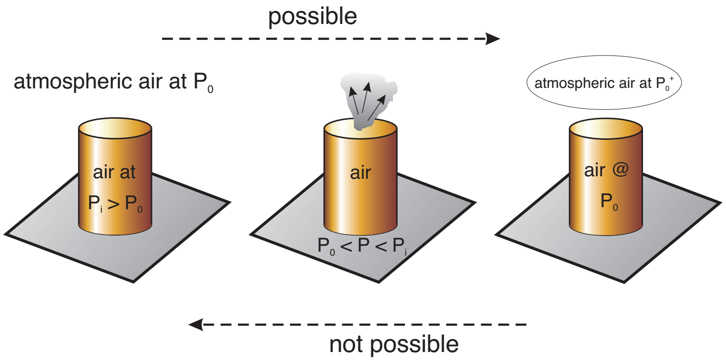
The 1st law allows many processes to occur spontaneously in either direction, but our experience tells us that they are not reversible.

Case 1: Hot object cooling down in atmosphere



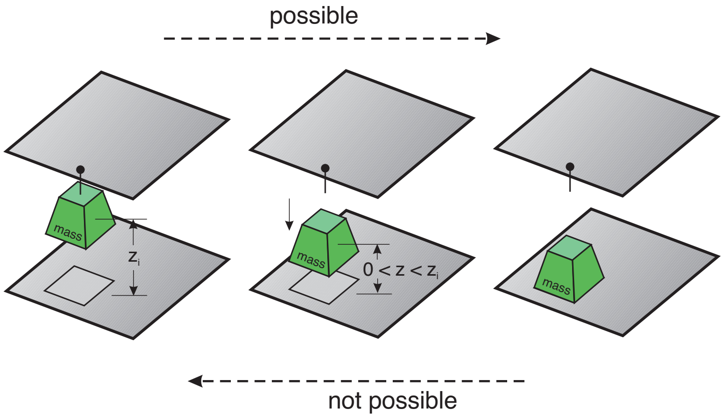
- object at T_i dissipates heat to the atmosphere at T_0 over time
- this process is <u>not</u> <u>reversible</u> i.e. energy dissipated to the atmosphere cannot be used to heat the object back to T_i

Case 2: Pressurized cylinder releases air to the environment



- air held at P_i in a closed tank is spontaneously released to the surroundings
- this process is <u>not reversible</u> i.e. atmospheric air will not spontaneously charge the tank even though energy is conserved

Case 3: A mass is allowed to fall from z_i

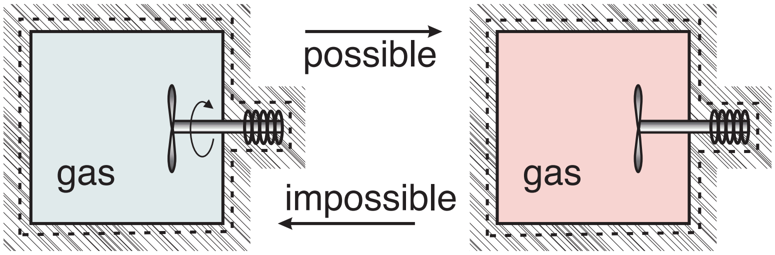


- a mass suspended by a cable at elevation z_i is released and allowed to fall
- this process is <u>not reversible</u> i.e. potential energy lost to internal energy via heating and compression cannot be used to raise the object

While the 1st law allowed us to determine the quantity of energy transfer in a process it does not provide any information about the direction of energy transfer nor the quality of the energy transferred in the process. In addition, we can not determine from the 1st law alone whether the process is possible or not. The second law will provide answers to these unanswered questions.

1. **Direction:**

   Consider an isolated system where $Q = W = 0$ (Assume energy to drive the propeller is a tensioned spring, and no work crosses the boundary.)



State 1: cold system,
rotating propeller
& gas

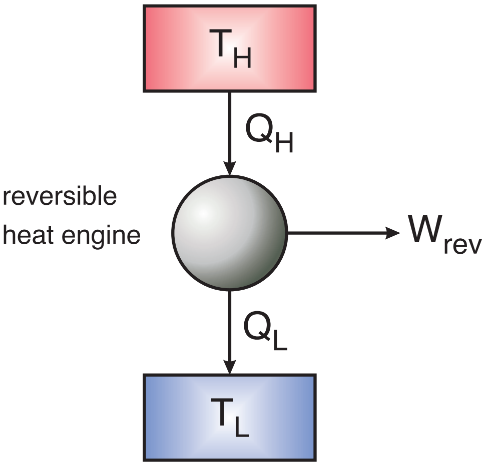
State 2: warm system,
stationary propeller
& gas

2. **Quality of Energy:**

   A heat engine produces reversible work as it transfers heat from a high temperature reservoir at T_H to a low temperature reservoir at T_L. If we fix the low temperature reservoir at $T_L = 300\ K$, we can determine the relationship between the efficiency of the heat engine,

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

   as the temperature of the high temperature reservoir changes. In effect we are determining the quality of the energy transferred at high temperature versus that transferred at low temperature.



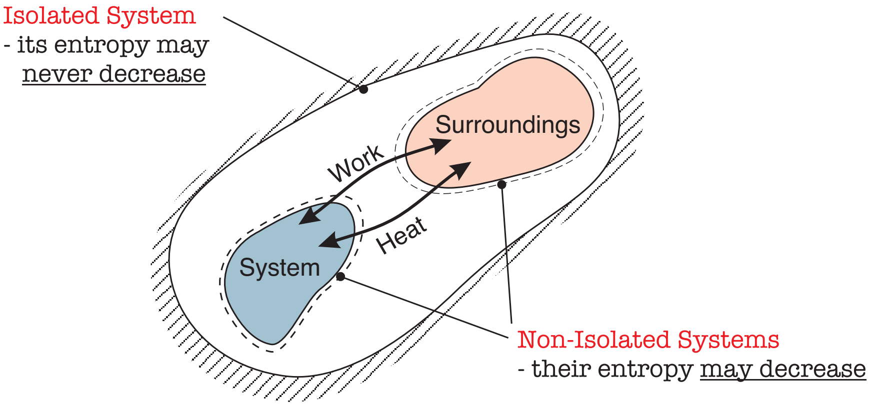
Second Law of Thermodynamics

Definition

> *The entropy of an isolated system can never decrease. When an isolated system reaches equilibrium, its entropy attains the maximum value possible under the constraints of the system*

- we have conservation of mass and energy, but not entropy. Entropy is not conserved.

- the 2nd law dictates why processes occur in a specific direction i.e., S_{gen} cannot be $-ve$
- the second law states: $(\Delta S)_{system} + (\Delta S)_{surr.} \geq 0$. If heat is leaving the system, then ΔS_{system} can be negative but the combined entropy of the system and the surroundings can never be negative.



Entropy

1. Like mass and energy, every system has entropy.

   Entropy is a measure of the degree of microscopic disorder and represents our uncertainty about the microscopic state.

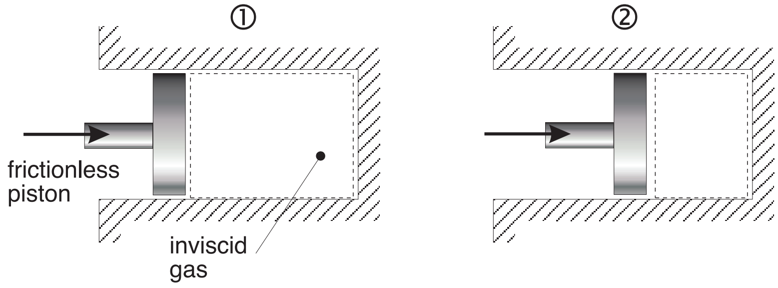
2. ***Reference:*** At $T = 0\ K\ S = 0$. There is no uncertainty about the microscopic state.
3. ***Relationship to Work:*** Microscopic disorder results in a loss of ability to do useful work.
4. ***Work:*** Energy transfer by work is microscopically organized and therefore entropy-free.
5. ***Heat:*** Energy transfer as heat takes place as work at the microscopic level but in a random, disorganized way. This results in entropy flow in or out of the system.

Reversible Process

In a reversible process things happen very slowly, without any resisting force, without any space limitation → *Everything happens in a highly organized way* (it is not physically possible - it is an idealization).

An internally reversible system is one in which there are no irreversibilities in the system itself but there may be irreversibilities in the surroundings such as in the transfer of heat across a finite temperature difference between the system and the surroundings.

Example: Slow adiabatic compression of a gas



Idealization - which makes the process completely reversible

$\rightarrow$ idealization where $S_2 = S_1 \;\; \Rightarrow \;\; S_{gen} = 0$

$T_2 > T_1 \quad \Rightarrow \quad$ increased microscopic disorder

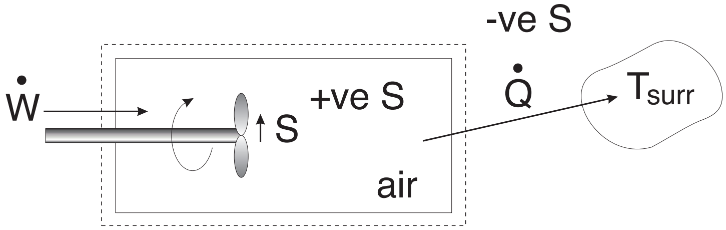
$V_2 < V_1 \quad \Rightarrow \quad$ reduced uncertainty about the whereabouts of molecules

$$\underbrace{Reversible}_{S_{gen}=0} + \underbrace{Adiabatic\ Process}_{Q=0} \Rightarrow \underbrace{Isentropic\ Process}_{S_1=S_2}$$

Does:

$$Isentropic\ Process \Rightarrow Reversible\ +\ Adiabatic$$

NOT ALWAYS - the entropy increase of a substance during a process as a result of irreversibilities may be offset by a decrease in entropy as a result of heat losses.



If $\dot{S}_{gen} = \dfrac{\dot{Q}}{T_{sur}}$, and

$\dot{S}_{gen} \;\; > \;\; 0$ (fluid friction)

$\Rightarrow$ not reversible

$\dot{Q} \;\; > \;\; 0 \quad \Rightarrow$ (non-adiabatic system)

If $\dot{S}_{gen}$ and $\dot{Q}/T_{TER}$ and $\Delta S = 0$, i.e. the system is isentropic, however, the system is not adiabatic nor is it reversible.

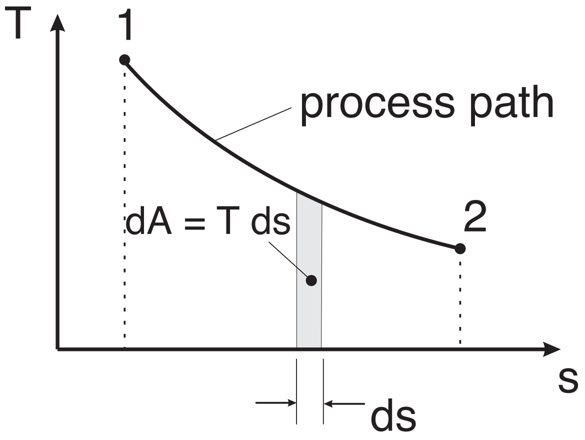
Evaluating Entropy

For a simple compressible system, Gibb's equations are given as:

$$Tds = du + Pdv$$

$$Tds = dh - vdP$$

- these relations are valid for open and closed, and reversible and irreversible processes



- the area under the curve on a $T - s$ diagram is the heat transfer for internally reversible processes

$$q_{int,rev} = \int_1^2 T\, ds$$

$$q_{int,rev,isothermal} = T\Delta s$$

- one can use Tds relations to calculate ds and Δs

Tabulated Calculation of Δs for Pure Substances

Calculation of the Properties of Wet Vapor:

Use Tables A-4 and A-5 to find $s_f,\ s_g$ and/or s_{fg} for the following

$$s = (1 - x)s_f + xs_g \qquad\qquad s = s_f + xs_{fg}$$

Calculation of the Properties of Superheated Vapor:

Given two properties or the state, such as temperature and pressure, use Table A-6.

Calculation of the Properties of a Compressed Liquid:

Use Table A-7. In the absence of compressed liquid data for a property $s_{T,P} \approx s_{f@T}$

Calculation of Δs for Incompressible Materials

$Tds = du + Pdv$ for an incompressible substance, $dv = 0$, and $C_p = C_v = C$

$$ds = \frac{du}{T} = C\frac{dT}{T} \Rightarrow \quad s_2 - s_1 = \int_1^2 C(T)\,\frac{dT}{T}$$

$$\Delta s = C_{avg} \ln \frac{T_2}{T_1} \qquad \text{where} \quad C_{avg} = [C(T_1) + C(T_2)]/2$$

- if the process is isentropic, then $T_2 = T_1$, and $\Delta s = 0$

Calculation of Δs for Ideal Gases

$$\begin{array}{lcrcl} \textbf{Ideal Gas Equation} & \Rightarrow & Pv & = & RT \\ du = C_v\, dT & \Rightarrow & u_2 - u_1 & = & C_v(T_2 - T_1) \\ dh = C_p\, dT & \Rightarrow & h_2 - h_1 & = & C_p(T_2 - T_1) \end{array}$$

There are 3 forms of a change in entropy as a function of T & v, T & P, and P & v.

$$\begin{aligned} s_2 - s_1 &= C_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1} \\ &= C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \\ &= C_p \ln \frac{v_2}{v_1} + C_v \ln \frac{P_2}{P_1} \end{aligned}$$

Variable Specific Heat

If we don't assume C_v and C_p to be constant i.e. independent of T, then we can use the ideal gas tables (Table A-21) as follows

$$\begin{aligned} s_2 - s_1 &= s^o(T_2) - s^o(T_1) + R \ln(v_2/v_1) \qquad \text{or} \\ s_2 - s_1 &= s^o(T_2) - s^o(T_1) - R \ln(P_2/P_1) \end{aligned}$$

Non-Reversible Processes and Isentropic Efficiencies

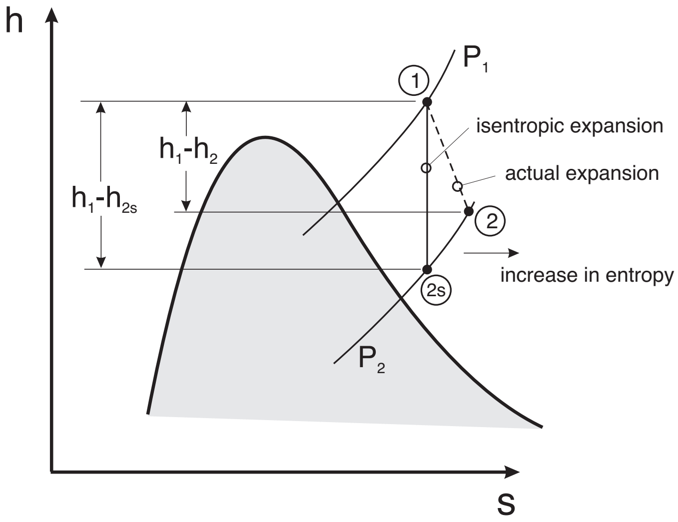
Real processes, such as expansion of steam in a turbine, produce irreversibilities associated with friction, mixing, etc. The net result is that the performance is downgraded, resulting in a loss of net work output attributed to an increase in entropy.

For a turbine under steady flow conditions, the theoretical maximum work output assuming no internal irreversibilities for an adiabatic process, i.e. isentropic expansion is

$$w_{isentropic} = h_1 - h_{2s}$$

However for a real process where expansion leads to an increase in entropy, the actual work output is degraded

$$w_{actual} = h_1 - h_2$$



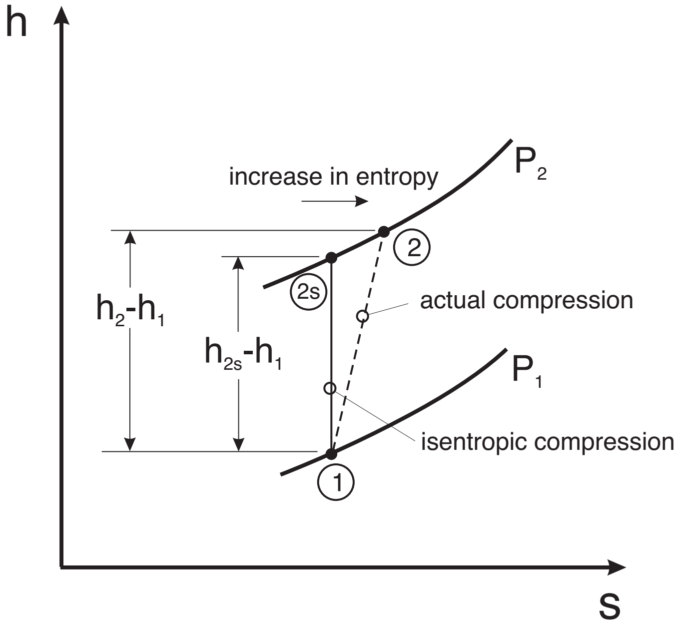
Work Output Devices: i.e. Turbines and Nozzles

The ratio of the actual work to the isentropic work is called the isentropic efficiency and is defined as follows:

Turbine:

$$\begin{aligned}\eta_T &= \frac{\text{actual turbine work}}{\text{isentropic turbine work}}\\ &= \frac{\boldsymbol{h_1 - h_2}}{\boldsymbol{h_1 - h_{2s}}}\end{aligned}$$

In a similar manner, the isentropic efficiency for other steady flow devices can be defined as follows:



Work Input Devices: i.e. Compressors and Pumps

Compressor:

$$\begin{aligned}\eta_C &= \frac{\text{Isentropic compressor work}}{\text{actual compressor work}}\\ &= \frac{\boldsymbol{h_{2s} - h_1}}{\boldsymbol{h_2 - h_1}}\end{aligned}$$

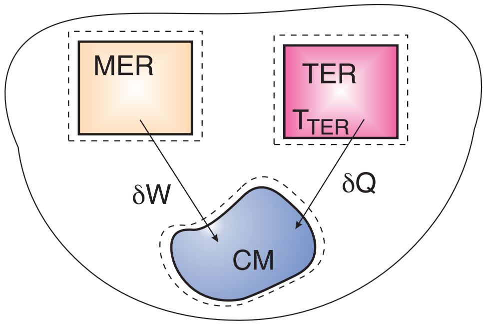
Pump:

$$\begin{aligned}\eta_P &= \frac{\text{Isentropic pump work}}{\text{actual pump work}}\\ &= \frac{\boldsymbol{h_{2s} - h_1}}{\boldsymbol{h_2 - h_1}}\end{aligned}$$

Nozzle:

$$\eta_N = \frac{\text{actual KE at nozzle exit}}{\text{Isentropic KE at nozzle exit}} = \frac{\boldsymbol{V_2^2}}{\boldsymbol{V_{2s}^2}} = \frac{\boldsymbol{h_1 - h_2}}{\boldsymbol{h_1 - h_{2s}}}$$

Entropy Balance for a Closed System (Control Mass)



We can first perform a 1st law energy balance on the system shown above.

$$dU = \delta Q + \delta W \qquad (1)$$

For a simple compressible system

$$\delta W = -PdV \qquad (2)$$

From Gibb's equation we know

$$T_{TER}\, dS = dU + PdV \qquad (3)$$

Combining (1), (2) and (3) we get

$$T_{TER}\, dS = \delta Q$$

net in-flow $\qquad dS = \dfrac{\delta Q}{T_{TER}}$

net out-flow $\qquad dS = -\dfrac{\delta Q}{T_{TER}}$

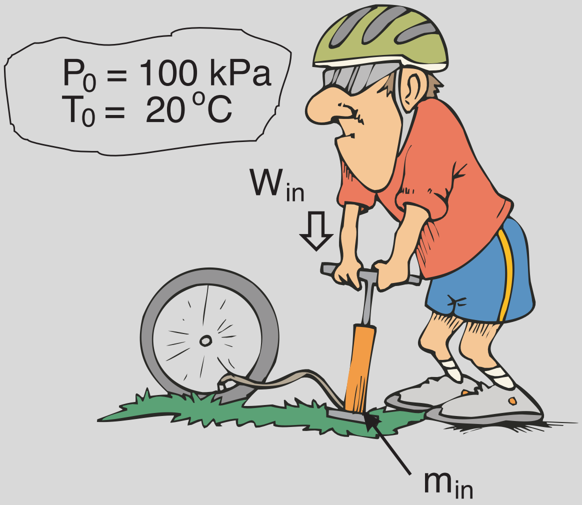
From the Clausius inequality we can show that the irreversibilities in the system lead to entropy production and the entropy balance equation becomes

$$\begin{aligned}
\underbrace{(dS)_{CM}}_{\equiv\, storage} &= \underbrace{\frac{\delta Q}{T_{TER}}}_{\equiv\, entropy\ flow} + \underbrace{dS_{gen}}_{\equiv\, production} \\
(S_2 - S_1)_{CM} &= \frac{Q_{1-2}}{T_{TER}} + \underbrace{S_{gen}}_{\geq 0} \\
accumulation &= (OUT - IN) + generation
\end{aligned}$$

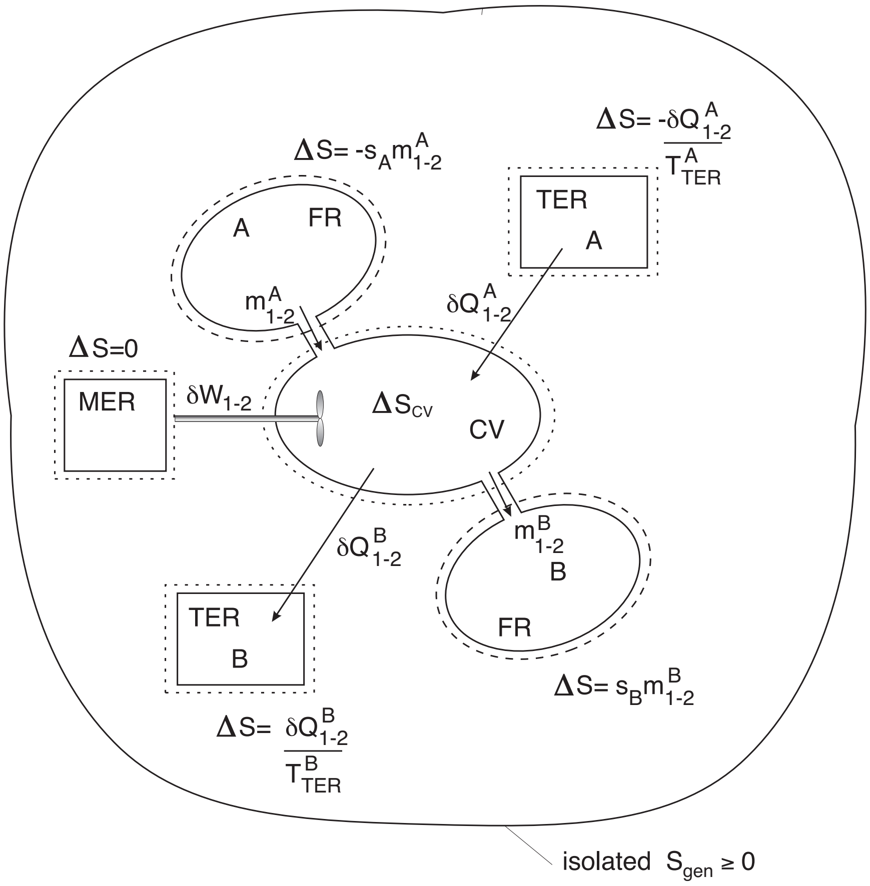
$\dfrac{Q_{1-2}}{T_{TER}}$ - the entropy associated with heat transfer across a finite temperature difference, i.e. $T > 0$

Example 4-1: A bicycle tire has a volume of $\boldsymbol{1200\ cm^3}$ which is considered to be constant during "inflation". Initially the tire contains air at atmospheric conditions given as $\boldsymbol{P_0 = 100\ kPa}$ and $\boldsymbol{T_0 = 20\ ^\circ C}$. A student then hooks up a bicycle pump and begins to force air from the atmosphere into the tire. After pumping stops and a new equilibrium is reached, the tire pressure is $\boldsymbol{600\ kPa}$ and the air temperature in the tire is $\boldsymbol{20\ ^\circ C}$.

a) Determine the mass $[\boldsymbol{kg}]$ of air added to the tire.
b) Determine the minimum amount of work $[\boldsymbol{kJ}]$ required to reach this end state.
c) If more than the minimum work is actually used, where does this extra energy go? That is what becomes of the extra energy?



Entropy Rate Balance for Open Systems (Control Volume)



For the isolated system going through a process from $\mathbf{1} \rightarrow \mathbf{2}$

$$\delta S_{gen} = (\Delta S)_{sys} + (\Delta S)_{sur}$$

$$\delta S_{gen} = \underbrace{\Delta S_{CV}}_{system} + \underbrace{\left(-s_A m^A_{1-2} + s_B m^B_{1-2} - \frac{\delta Q^A_{1-2}}{T^A_{TER}} + \frac{\delta Q^B_{1-2}}{T^B_{TER}}\right)}_{surroundings}$$

or as a rate equation

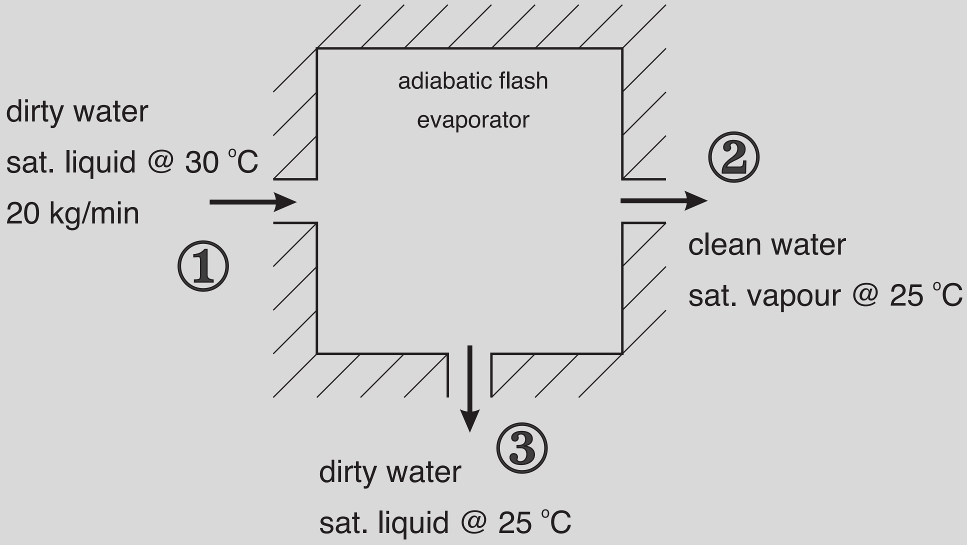
$$\dot{S}_{gen} = \left(\frac{dS}{dt}\right)_{CV} + \left(s\dot{m} + \frac{\dot{Q}}{T_{TER}}\right)_{OUT} - \left(s\dot{m} + \frac{\dot{Q}}{T_{TER}}\right)_{IN}$$

This can be thought of as

$$generation = accumulation + OUT - IN$$

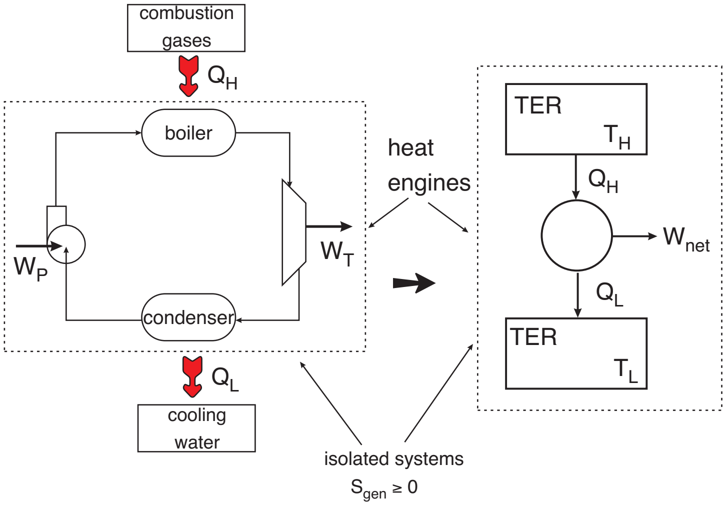
Example 4-2: An adiabatic flash evaporator is used to make a small amount of clean water from dirty water. The dirty water enters as saturated liquid at $30\ ^{\circ}C$ and at a rate of $20\ kg/min$. Clean water leaves as a saturated vapour at $25\ ^{\circ}C$. Dirty water leaves the evaporator as saturated liquid at $25\ ^{\circ}C$.

a) Determine the mass flow rate $[kg/min]$ of the clean water vapour.
b) Determine the rate of entropy generation $[kW/K]$ within the evaporator.



Entropy Generation in a System of Components: Heat Engine

A heat engine is a device in which a working substance (control mass) undergoes a cyclic process while operating between two temperature reservoirs (TER).



For the general case, the 1st law energy balance gives

$$\cancelto{0}{\Delta E} = Q_H - Q_L - W_{net} = 0 \qquad (1)$$

The 2nd law gives

$$S_{gen} \geq 0 \qquad \text{for an isolated system}$$

where $S_{gen} = 0$ implies a reversible system and $S_{gen} > 0$ implies a real system.

An entropy balance gives

$$S_{gen} = \underbrace{(\Delta S)_{CM}}_{\equiv 0\ (cyclic)} + \underbrace{(\Delta S)_{TER-H}}_{\equiv -Q_H/T_H} + \underbrace{(\Delta S)_{TER-L}}_{\equiv +Q_L/T_L} + \cancelto{0}{(\Delta S)_{MER}}$$

Therefore

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H} + \frac{S_{gen}\, T_L}{Q_H} \qquad (2)$$

Combining Eqs. (1) and (2)

$$\begin{aligned} W_{net} &= Q_H - Q_L = Q_H\left(1 - \frac{Q_L}{Q_H}\right) \\ &= Q_H\left(1 - \frac{T_L}{T_H} - \frac{S_{gen}\, T_L}{Q_H}\right) \\ &= \underbrace{Q_H\left(1 - \frac{T_L}{T_H}\right)}_{W_{max}\ \text{possible}} - \underbrace{T_L S_{gen}}_{W_{lost}\ \text{due to irreversibilties}} \end{aligned}$$

The engine efficiency is defined as the benefit over the cost

$$\eta = \frac{benefit}{cost} = \frac{W_{net}}{Q_H} = 1 - \frac{T_L}{T_H} - \frac{T_L S_{gen}}{Q_H}$$