Entropy and the Second Law of Thermodynamics

Reading	Problems
5-1 ⟶ 5-3, 5.6, 5.7	5-25, 5-71, 5-74
6-1 ⟶ 6-11	6-31, 6-33, 6-42, 6-57, 6-59, 6-65, 6-72, 6-77

Introduction

Zeroth Law: led to the concept of *temperature*

First Law: led to the thermodynamic property called *internal energy*

Second Law: leads to the thermodynamic property called *entropy*

Why do we need another law in thermodynamics?

Answer: 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.

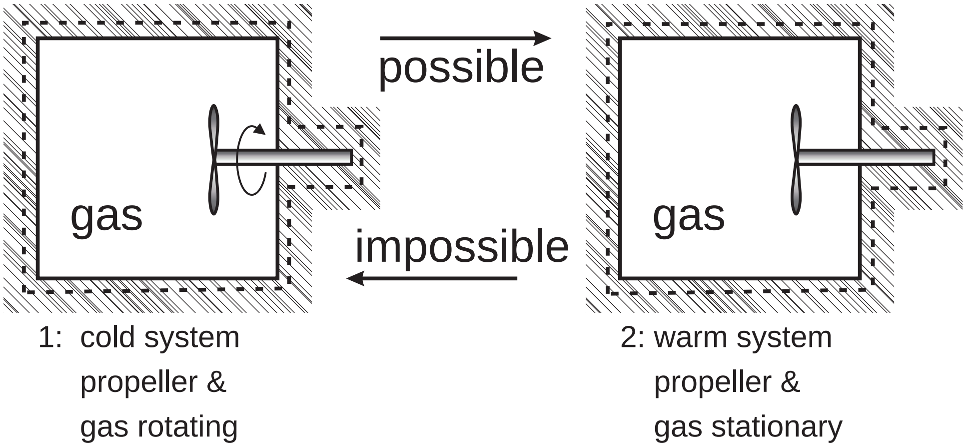
A process will not occur unless it satisfies both the first and the second laws of thermodynamics.

1. **Direction:**

   Consider an isolated system where $Q = W = 0$

   From the 1st law we know

$$\underbrace{(U + KE)_1}_{E_1} = \underbrace{U_2}_{E_2} \qquad \left\{ \begin{array}{c} \text{same both ways} \\ 1 \rightarrow 2 \\ 2 \rightarrow 1 \end{array} \right.$$



The physical interpretation of this is:

State 1: Most of the energy is in a highly organized form residing in the macroscopic KE of the propeller and the rotating gas.

State 2: All of the energy is now in a disorganized form residing in the microscopic E, i.e. U of the propeller and the gas.

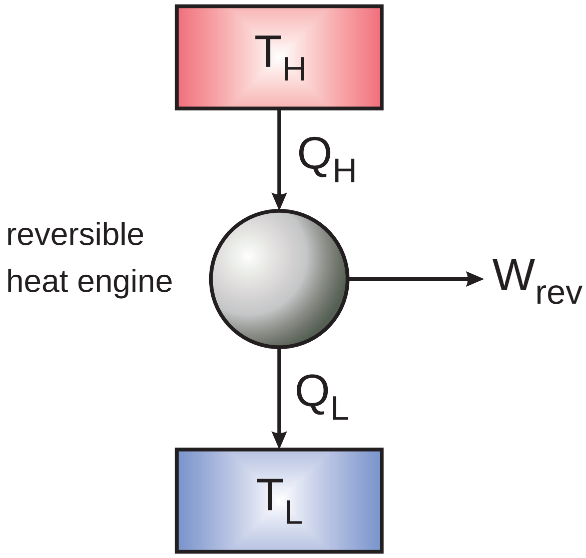
- The process $1 \longrightarrow 2$ has resulted in a higher state of molecular chaos. $ENTROPY$ is the thermodynamic property that describes the degree of molecular disorder in matter. Hence, $S_2 > S_1$. Entropy can be considered a quantitative index that describes the quality of energy.
- The process $2 \longrightarrow 1$ is impossible because it would require disorganized KE to produce macroscopically organized KE. That is $S_2 < S_1$ which is impossible for an isolated system.
- A thermodynamic process is only possible if it satisfies both the 1st and 2nd laws simultaneously.

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.



T_L (K)	T_H (K)	η
300	1000	0.700
300	800	0.625
300	600	0.500
300	400	0.250

Since the purpose of the heat engine is to convert heat energy to work energy, we can clearly see that more of the high temperature thermal energy can be converted to work. Therefore the higher the temperature, the higher the quality of the energy.

Second Law of Thermodynamics

The second law of thermodynamics states:

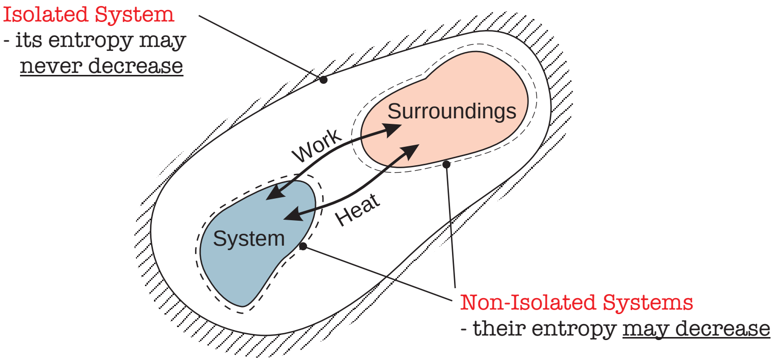
> *The entropy of an isolated system can never decrease. When an isolated system reaches equilibrium, its entropy attains the maximum value possible under the constraints of the system*

Definition

Unlike mass and energy, entropy can be produced but it can never be destroyed. That is, the entropy of a system plus its surroundings (i.e. an isolated system) can never decrease (2nd law).

$$\begin{aligned}
\mathcal{P}_m &= m_2 - m_1 = 0 \ \text{(conservation of mass)} \\
\mathcal{P}_E &= E_2 - E_1 = 0 \ \text{(conservation of energy)} \rightarrow \text{1st law} \\
\mathcal{P}_S &= S_{gen} = S_2 - S_1 \geq 0 \ \ \rightarrow \text{2nd law}
\end{aligned}$$

- 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 $-ve$
- S_{gen} is created by irreversibilities in a system, and therefore can be used to quantify the efficiency of a process. It is a measure of the perfectness of a process. The smaller S_{gen} is, the more efficient the process.
- if heat is leaving, then ΔS can be negative for a system. ΔS_{total} cannot be negative.



The second law states, for an isolated system:

$$(\Delta S)_{system} + (\Delta S)_{surr.} \geq 0$$

where $\Delta \equiv final - initial$

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:*** In a prefect crystal of a pure substance at $T = 0\ K$, the molecules are completely motionless and are stacked precisely in accordance with the crystal structure. Since entropy is a measure of microscopic disorder, then in this case $S = 0$. That is, there is no uncertainty about the microscopic state.

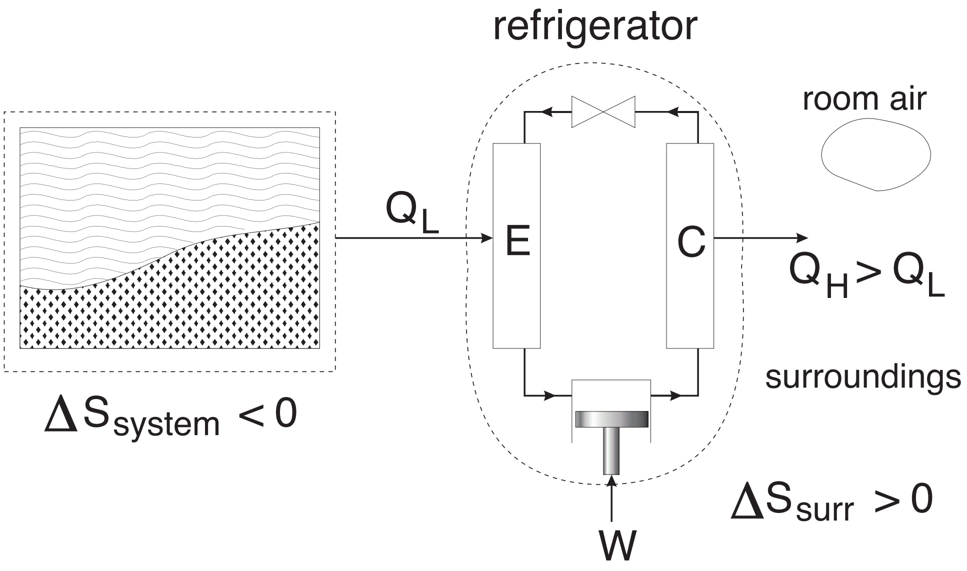
   Example: A freezing process

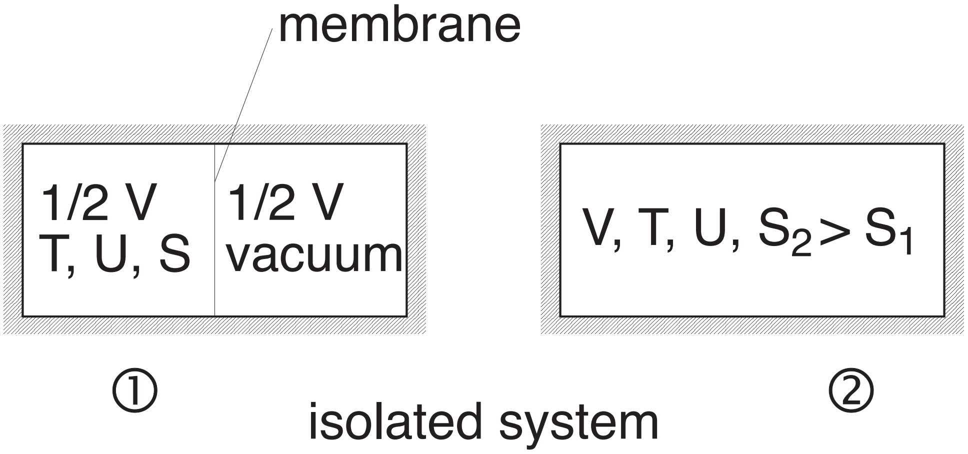
3. ***Relationship to Work:*** For a given system, an increase in the microscopic disorder (that is an increase in entropy) results in a loss of ability to do useful work. Work can completely (and easily) be transformed into thermal energy and then exchanged as heat.

   Example: Unrestrained expansion of an ideal gas

   A 1st law balance gives $U_1 = U_2$. For an ideal gas, we know $u = u(T)$ only and $T_1 = T_2$.

   The internal energy and the temperature of the gas remain unchanged but the gas in state 2 is in a more random or disordered state than 1 because now any gas molecules can move at





random within the whole volume V rather than $V/2$. In other words, uncertainty of a gas molecule has increased.

$$S_2 > S_1$$

The reverse process $2 \longrightarrow 1$ is extremely unlikely to occur because the probability of finding all of the gas molecules in $1/2V$ at an instant of time is extremely remote, although not zero. Hence the process is *irreversible*.

4. ***Work:*** Energy transfer by work is microscopically organized and therefore entropy-free. Work can completely (and easily) be transformed into thermal energy and then exchanged as heat.

5. ***Heat:*** Energy transfer as heat takes place as work at the microscopic level but in a random, disorganized way. This type of energy transfer carries with it some chaos and thus results

in entropy flow in or out of the system. Heat transfer from a heat source cannot be used to exchange the same amount of energy as work.

6. ***Reversibility:*** According to the 2nd law, no real process can be reversed without leaving any trace on the surroundings. In fact, the 2nd law says that it is impossible to do things perfectly (it is ideal but impossible). It is our job (as engineers) to make the process as close as possible to ideal, i.e. no loss and perfect recovery. A reversible process is the theoretical limit for an irreversible (real) process.

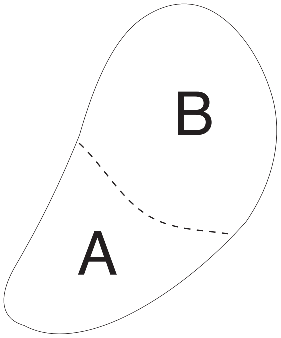
   Some factors that cause a process to become irreversible:

   - friction
   - unrestrained expansion and compression
   - mixing
   - heat transfer (finite ΔT)
   - elastic resistance
   - inelastic deformation
   - chemical reactions

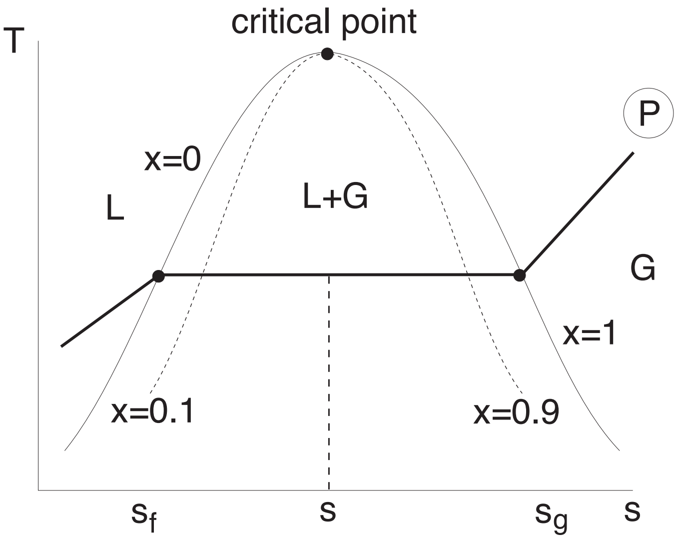
   In a reversible process things happen very slowly, without any resisting force, without any space limitation → *Everything happens in a highly organized way* (it is not physically possible - it is an idealization).

7. Entropy is an extensive property with the dimensions of energy/temperature

$$S : \frac{J}{K}$$



$$\begin{aligned} S &= S_A + S_B \\ &= m_A s_A + m_B s_B \end{aligned}$$



The $\boldsymbol{T - s}$ diagram

$$\boldsymbol{s = (1 - x)\, s_f + x\, s_g}$$

where $\boldsymbol{x}$ ⇒ quality ⟶ fraction of the total <u>mass</u> which is saturated **vapor**.

Gibb's Equation

From a 1st law energy balance when KE and PE are neglected

$$\boldsymbol{Energy\ Input = Energy\ Output\ +\ Increase\ in\ Energy\ Storage}$$

$$\underbrace{\delta Q}_{amount} = \delta W + \underbrace{dU}_{differential} \qquad (1)$$

We know that the differential form of entropy is

$$dS = \frac{\delta Q}{T} \qquad (2) \qquad\qquad \delta W = PdV \qquad (3)$$

Combining Eqs. 1, 2 and 3

$$dS = \frac{dU}{T} + \frac{PdV}{T} \quad \Rightarrow \quad \underbrace{ds = \frac{du}{T} + \frac{Pdv}{T}}_{\text{per unit mass}}$$

Alternate Derivation:

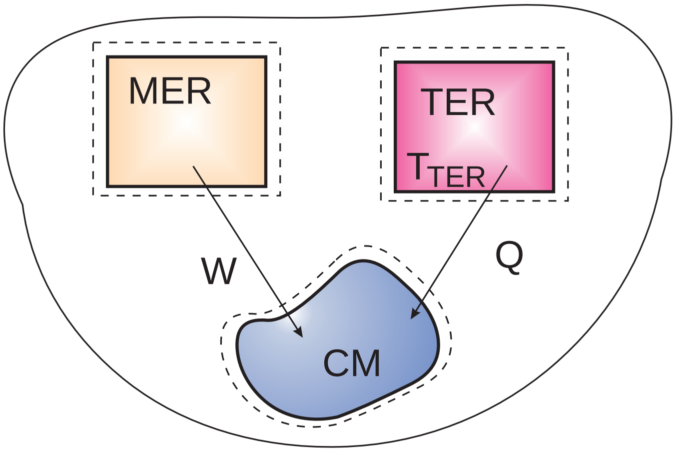
$$S = S(U, V)$$

$$dS = \underbrace{\left(\frac{\partial S}{\partial U}\right)_V}_{=\frac{1}{T}} dU + \underbrace{\left(\frac{\partial S}{\partial V}\right)_U}_{=\frac{P}{T}} dV$$

$$\boxed{T\,dS = dU\ +\ PdV}$$

This form of Gibb's equation is very general and very useful.

2nd Law Analysis 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

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

where

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

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

Therefore

$$\underbrace{(dS)_{CM}}_{\equiv\ storage} = \underbrace{\frac{\delta Q}{T_{TER}}}_{\equiv\ entropy\ flow} + \underbrace{d\mathcal{P}_S}_{\equiv\ production}$$

Integrating gives

$$(S_2 - S_1)_{CM} = \frac{Q_{1-2}}{T_{TER}} + \underbrace{S_{gen}}_{\geq 0}$$

where

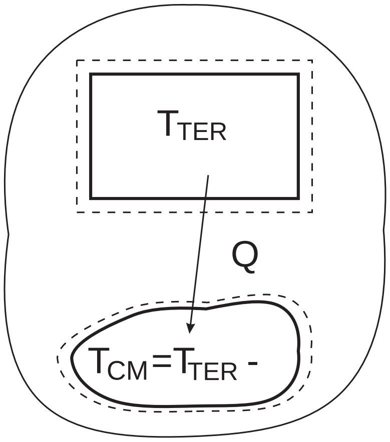
$\dfrac{Q_{1-2}}{T_{TER}}$ - the entropy associated with heat transfer across a finite temperature difference, i.e. $T > 0$

Question?

If all heat transfer processes are inherently irreversible ⟶ how can we speak of a reversible system involving heat transfer?

$$S_2 - S_1 = \frac{Q_{1-2}}{T_{TER}} + \underbrace{\cancelto{0}{S_{gen}}}_{(reversible)}$$

Possible only if Q occurs across an infinitesimal temperature difference, i.e. quasi-equilibrium



let $\epsilon = T_{TER} - T_{CM}$

$$S_{gen} = (dS)_{CM} + (dS)_{TER} = \frac{\delta Q}{(T_{TER} - \epsilon)} + \frac{\delta Q}{T_{TER}}$$

as $\epsilon \longrightarrow 0$ then $S_{gen} \longrightarrow 0$.

Thus

$$(dS)_{CM} \approx \frac{\delta Q}{T_{TER}} \approx \frac{\delta Q}{T_{CM}}$$

In summary, $\delta Q = T\ dS$ for a slow heat transfer process across a infinitesimal temperature difference, therefore we can assume that it is a reversible process.

Why use T_{TER} as the sink temperature regardless of the direction of heat flow?

Lets examine heat transfer from system A to system B, where system A is at T_{TER} and system B is changing in temperature as heat is transferred.

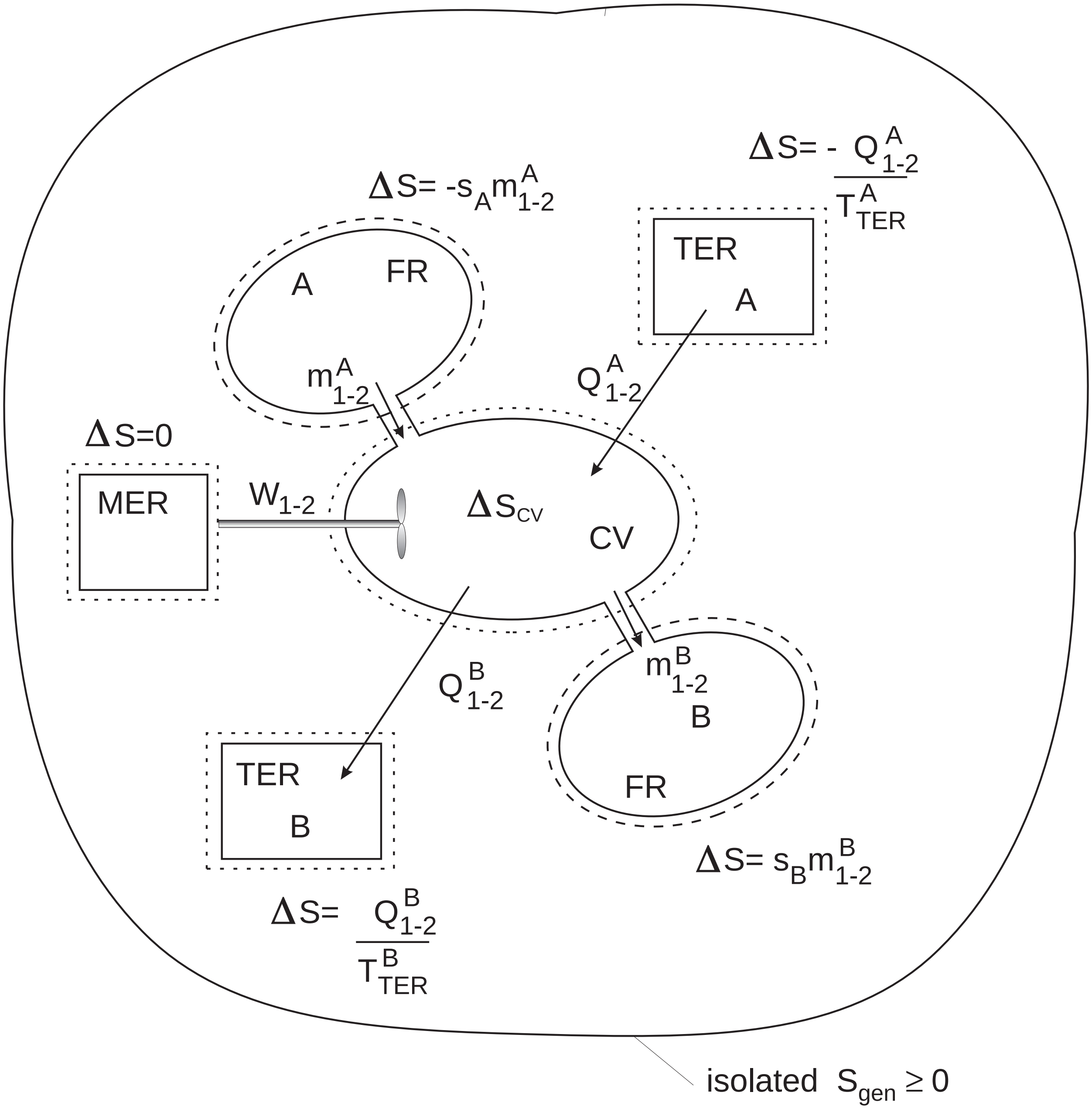
$$(S_2 - S_1) = \left(\int_1^2 \frac{Q}{T}\right)_A = \left(-\int_1^2 \frac{Q}{T}\right)_B$$

If the system is externally reversible $\longrightarrow$ there are no other additions of S other than the heat transfer process. Therefore the magnitude of the entropy transfer is identical regardless of the sink temperature used, only the sign changes.

Since $T_A = T_{TER}$ is constant it is convenient to use the form that allows us to use the constant temperature process (avoiding integration where we would have to monitor the temperature change in B), therefore we can say

$$\Delta S = \frac{Q_{1-2}}{T_{TER}}$$

2nd Law Analysis for Open Systems (Control Volume)



where:

FR - fluid reservoir
TER - thermal energy reservoir
MER - mechanical energy reservoir

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

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

$$\delta S_{gen} = \underbrace{\Delta S_{CV}}_{system} + \underbrace{\left(-s_A m_{1-2}^A + s_B m_{1-2}^B - \frac{\delta Q_{1-2}^A}{T_{TER}^A} + \frac{\delta Q_{1-2}^B}{T_{TER}^B}\right)}_{surroundings}$$

or as a rate equation

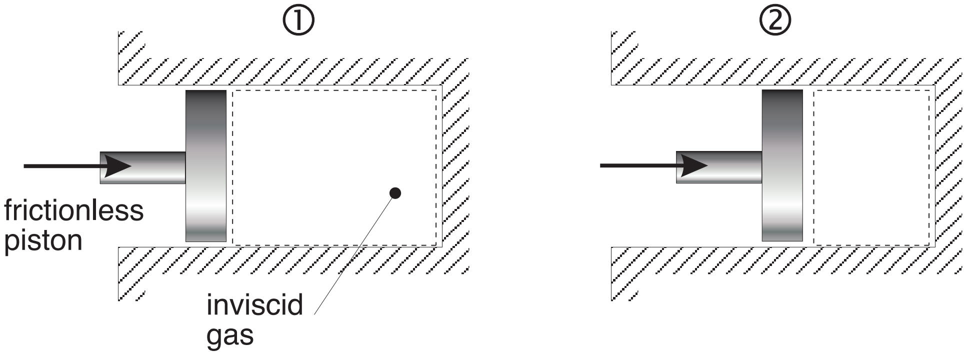
$$\dot{S}_{gen} = \left(\frac{dS}{dt}\right)_{CV} + \left(s\dot{m} + \frac{\dot{Q}}{T_{TER}}\right)_{OUT} - \left(s\dot{m} + \frac{\dot{Q}}{T_{TER}}\right)_{IN}$$

This can be thought of as

$$generation = accumulation + OUT - IN$$

Reversible Process

Example: Slow adiabatic compression of a gas



Idealization - which makes the process completely reversible

A process $\mathbf{1} \longrightarrow \mathbf{2}$ is said to be reversible if the reverse process $\mathbf{2} \longrightarrow \mathbf{1}$ restores the system to its original state without leaving any change in either the system or its surroundings.

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

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

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

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

The 2nd law states:

$$(\Delta S)_{system} + (\Delta S)_{surr} = S_{gen} \geq 0$$

where:

> 0 irreversible (real world)

$= 0$ reversible (frictionless, perfectly elastic, inviscid fluid)

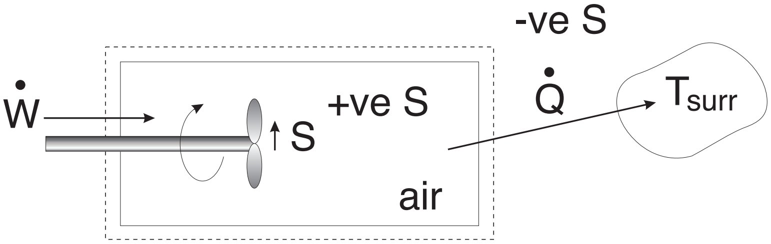
- for all real processes, the entropy of a closed system (i.e. the universe) is continuously increasing. The best scenario, a reversible world.

- the closest man has gotten to a reversible process is with charge flow through superconductors at very low temperatures (approaching $\boldsymbol{0\ K}$).
- bad for engineers because good quality energy is disappearing
- physicists use this argument to prove that the universe will eventually die
- mathematicians have chaos theory

But does:

$$\boldsymbol{Isentropic\ Process \Rightarrow Reversible\ +\ Adiabatic}$$

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.



At steady state:

$$\boldsymbol{\dot{W} = \dot{Q} \quad (1st\ law)}$$

$$\boldsymbol{S_{CV} = constant \Rightarrow isentropic}$$

From the 2nd law

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

but

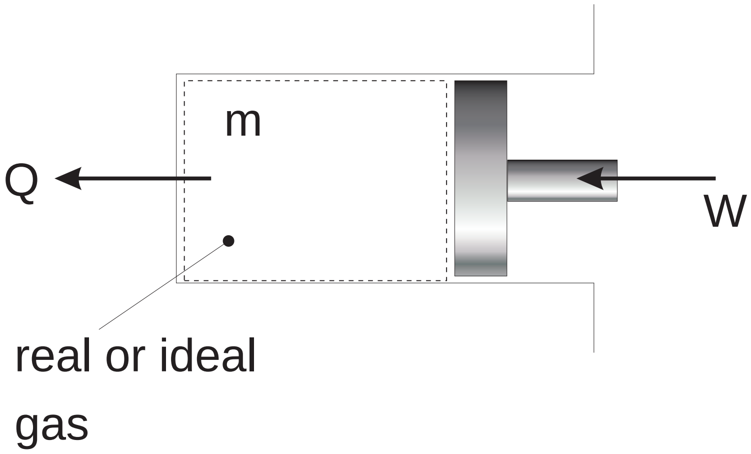
$$\begin{aligned} \frac{d}{dt}S_{CV} &= 0 \text{ (steady state)} \\ \dot{m}s &= 0 \text{ (no flow)} \\ \frac{\dot{Q}}{T_{TER}} &= 0 \text{ (no heat transfer in)} \end{aligned}$$

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

$$\begin{aligned} \dot{S}_{gen} &> 0 \text{ (fluid friction)} \\ \dot{Q} &> 0 \text{ (non-adiabatic system)} \end{aligned}$$

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.

Reversible Compression and Expansion



From the 1st law

$$\begin{aligned} \text{increase in energy storage} &= \text{energy input} \\ dU &= \delta W - \delta Q \\ mdu &= \delta W - \delta Q \qquad (1) \end{aligned}$$

From the 2nd law for a control mass

$$dS = -\frac{\delta Q}{T} + S_{gen}$$

where $S_{gen} = 0$ for a reversible process.

Therefore

$$mds = -\frac{\delta Q}{T} \qquad (2)$$

Combining (1) and (2) through the $-\delta Q$ term gives

$$mdu = \delta W + mTds \qquad (3)$$

From Gibb's Eq.

$$\begin{aligned} Tds &= du + Pdv \\ mdu &= mTds - mPdv \qquad (4) \end{aligned}$$

Combining Eqs. (3) and (4)

$$\begin{aligned} mTds - mPdv &= \delta W + mTds \\ \delta W &= -mPdv \end{aligned}$$

Integrating gives

$$W_{1-2} = -m\int_1^2 Pdv$$

or on a per unit mass basis

$$\boxed{w_{1-2} = \frac{W_{1-2}}{m} = -\int_1^2 Pdv}$$

Good for:

- reversible process
- any gas, real or ideal

Reversible Isothermal Expansion for an Ideal Gas

We know for an ideal gas

$$Pv = constant = RT$$

or

$$P = \frac{constant}{v} \qquad (1)$$

$$Pv = constant = P_1 v_1 = P_2 v_2 \qquad (2)$$

The work done at the boundary of a simple, compressible substance (S.C.S.) during a reversible process

$$\begin{aligned} w_{1-2} = -\int_1^2 P dv &= -constant \int_1^2 \frac{dv}{v} \\ &= -P_1 v_1 \ln \frac{v_2}{v_1} \\ &= P_1 v_1 \ln \frac{v_1}{v_2} \end{aligned}$$

$$\begin{aligned} W_{1-2} = mRT \ln \frac{v_1}{v_2} &= mRT \ln \frac{V_1}{V_2} \\ &= mRT \ln \frac{P_2}{P_1} \end{aligned}$$

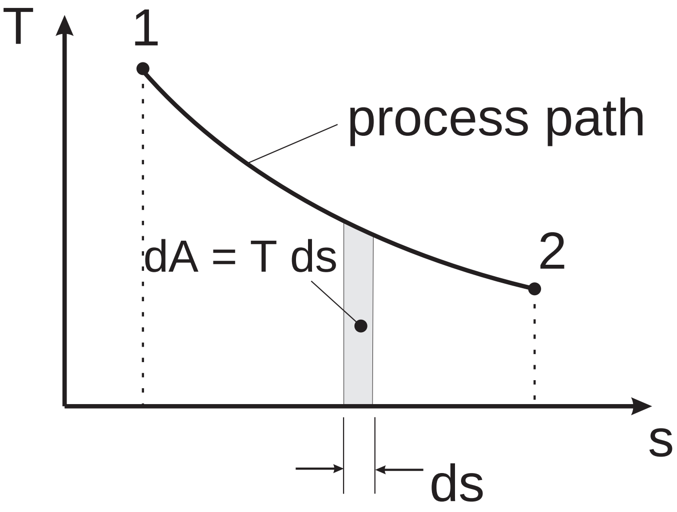
Calculation of Δs in Processes

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

$$\begin{aligned} Tds &= du + Pdv \\ Tds &= dh - vdP \end{aligned}$$

- these relations are valid for open and closed, and reversible and irreversible processes
- ds can be solved by integrating the equations in combination with other known relations ($dh = C_p dT,\ du = C_v dT,\ Pv = RT$, etc)
- an adiabatic and reversible process must also be an isentropic process ($\Delta s = 0$) (but not visa versa)
- $T - s$ and $h - s$ (Mollier) diagrams are very useful
  - the area under the curve on a $T - s$ diagram is the heat transfer for internally reversible processes

$$q_{int,rev} = \int_1^2 T\, ds \qquad \text{and} \qquad q_{int,rev,isothermal} = T\Delta s$$



  - Notes:
    - $*$ it is not good to attribute a value to s at a specific state
    - $*$ as before, we must assign a reference state where $s = 0$ (i.e. for water, we use the triple point)
    - $*$ one can use Tds relations to calculate ds and Δs
    - $*$ we can deal with s exactly as we deal with h and u

Tabulated Calculation of Δs for Pure Substances

Depending on the phase of the substance:

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

$Tds = du + Pdv$ (the other $T\ ds$ equation reduces the same way)

- for an incompressible substance, $dv = 0$, and $C_p = C_v = C$

$$\begin{aligned} ds &= \frac{du}{T} = C\frac{dT}{T} \\ s_2 - s_1 &= \int_1^2 C(T)\,\frac{dT}{T} \\ \Delta s &= C_{avg} \ln\frac{T_2}{T_1} \qquad \text{where} \quad C_{avg} = [C(T_1) + C(T_2)]/2 \end{aligned}$$

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

Calculation of Δs for Ideal Gases

For an ideal gas with constant C_p and C_v

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

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

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

with the gas constant R given as

$$R = C_p - C_v$$

The equations for Δs in an ideal gas can be readily attained by combining Gibb's equation, the Ideal gas law and the differential form of internal energy and entropy as follows:

Δs for T and v given:

From Gibb's Equation

$$ds = \frac{du}{T} + \frac{P}{T}dv = C_v\frac{dT}{T} + R\frac{dv}{v}$$

where from the ideal gas equation

$$\frac{P}{T} = \frac{R}{v}$$

and $du = C_v\,dT$.

If we integrate ds, we obtain

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

Δs for T and P given:

Noting that

$$dh = du + Pdv + vdP$$

we can substitute into ds to get

$$\begin{aligned} ds = \frac{dh}{T} - \frac{P}{T}dv - \frac{v}{T}dP + \frac{P}{T}dv &= \frac{dh}{T} - \frac{v}{T}dP \\ &= C_p\frac{dT}{T} - R\frac{dP}{P} \\ &= C_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right) \end{aligned}$$

Δs for P and v given:

And finally,

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

where

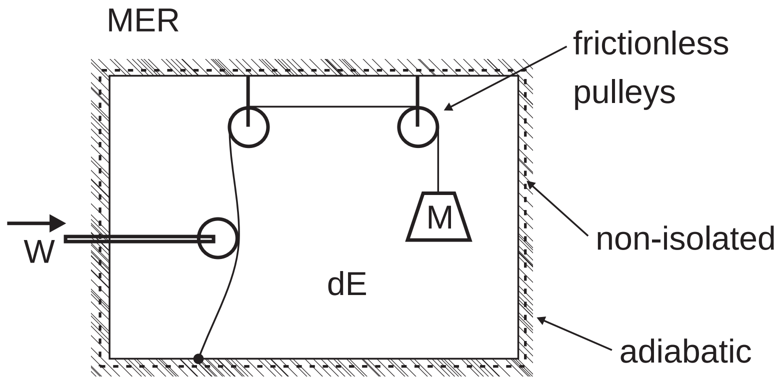
$$\frac{T_2/v_2}{T_1/v_1} = \frac{P_2/R}{P_1/R} = P_2/P_1$$

System Level Analysis

Energy Reservoirs

Idealized Mechanical Energy Reservoir (MER)

This is a source or sink for organized energy.

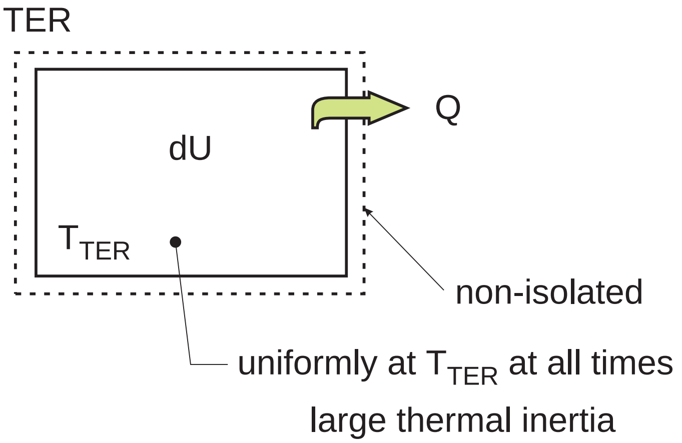


The system shown above is open to work transfer only, therefore it is entropy free.

$$dS = 0 \qquad \text{for a MER}$$

Idealized Thermal Energy Reservoir (TER)

This is a source or sink for disorganized energy.

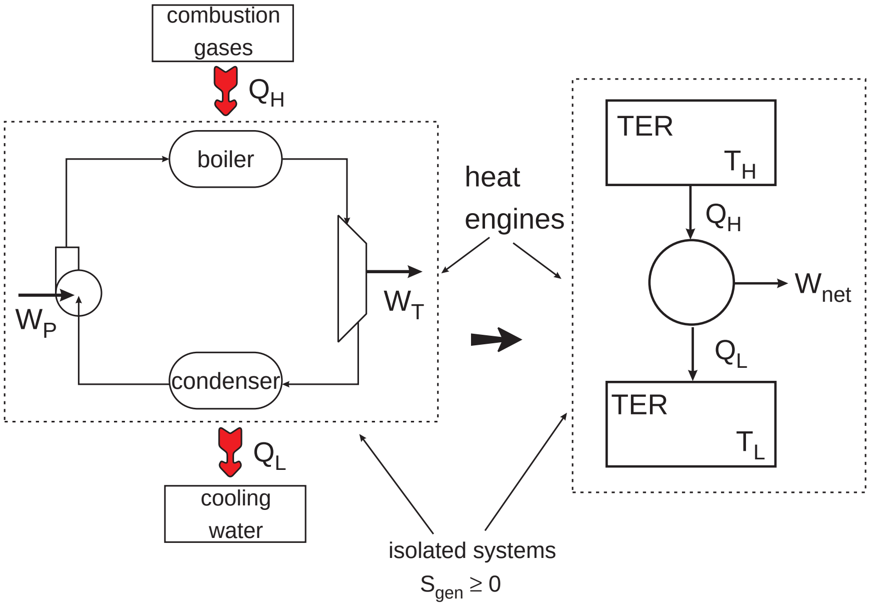


Examples include; oceans, rivers, lakes, the atmosphere, etc.

Reversible 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).

As an example we can simplify the conventional power plant where a fossil fuel or a nuclear process is used to provide high temperature energy to a boiler. Through a vapor compression/expansion process, mechanical energy is produced in a turbine that in turn is used to produce electrical energy.



Find:

1. $\boldsymbol{W_{net} = W_T - W_p = ?}$
2. $\boldsymbol{W_{net,max} = ?}$
3. $\boldsymbol{\eta_{max}}$

Solution:

A 1st law energy balance gives

$$\Delta \cancel{E}^{0} = Q_H - Q_L - W_{net} = 0 \quad (1)$$

The 2nd law gives

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

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

$$\frac{Q_L}{T_L} = \frac{Q_H}{T_H} + S_{gen}$$

or

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

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

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

For a perfect (reversible) system where $S_{gen} = 0$

$$\eta = 1 - \frac{T_L}{T_H} \quad \Leftarrow \quad \text{Carnot efficiency}$$

It is clear that even for a “perfect” the efficiency cannot be 100%

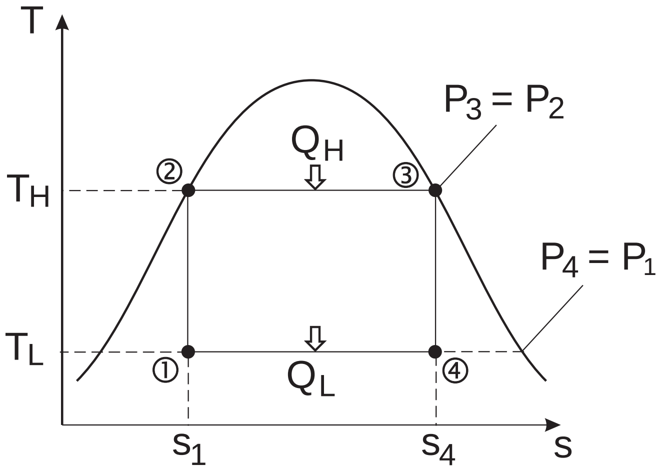
If we were to assume an ambient temperature of $\boldsymbol{T_L = 293\ K}$ and $\boldsymbol{T_H = 1000\ K}$, which is roughly equivalent to the maximum temperature of high grade metals, then

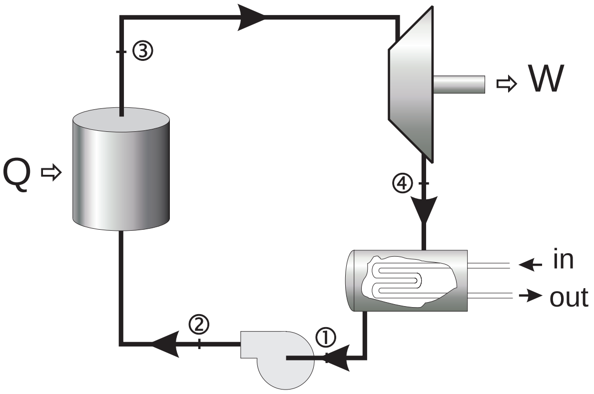
$$\boldsymbol{\eta_{max} = 1 - \frac{293}{1000} \approx 71\%}$$

In reality most heat engines have an efficiency of less that $\boldsymbol{40\%}$ due to irreversibilities.

The Carnot Cycle

- an ideal theoretical cycle that is the most efficient conceivable
- based on a fully reversible heat engine - it does not include any of the irreversibilities associated with friction, viscous flow, etc.
- in practice the thermal efficiency of real world heat engines are about half that of the ideal, Carnot cycle





Process	State Points	Description
Pump	1 ⟶ 2	isentropic compression from $T_L \longrightarrow T_H$ to return vapor to a liquid state
Heat Supply	2 ⟶ 3	heat is supplied at constant temperature and pressure
Work Output	3 ⟶ 4	the vapor expands isentropically from the high pressure and temperature to the low pressure
Condenser	4 ⟶ 1	the vapor which is wet at 4 has to be cooled to state point 1

The cycle is totally reversible.

The reversed Carnot cycle is called the Carnot refrigeration cycle.

Cycle Efficiency

- defined as the net work output divided by the gross heat supplied

$$\begin{aligned}\eta &= \frac{W_{net}}{Q_H} \\ &= \frac{Q_H - Q_L}{Q_H} \\ &= 1 - \frac{T_L}{T_H}\end{aligned}$$

From the figure the gross heat supplied is

$$Q_H = area(s_1 \longrightarrow s_4 \longrightarrow 3 \longrightarrow 2 \longrightarrow s_1) = T_H(s_4 - s_1)$$

The net work output is

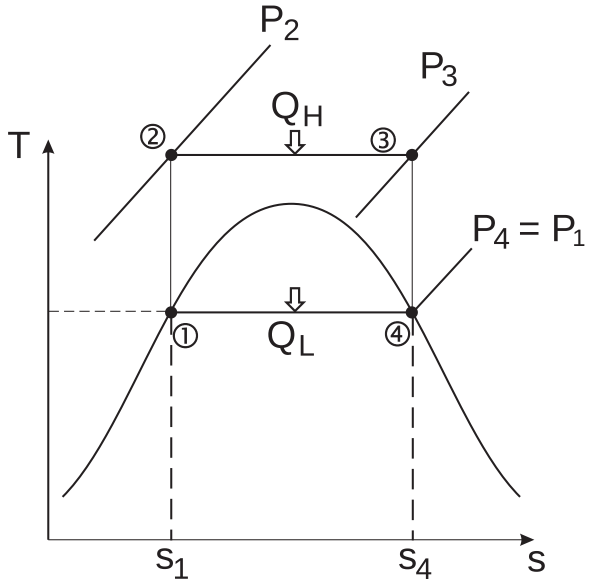
$$Q_H - Q_L = area(1 \longrightarrow 4 \longrightarrow 3 \longrightarrow 2) = (T_H - T_L)(s_4 - s_1)$$

Therefore the Carnot efficiency is

$$\eta = \frac{(T_H - T_L)(s_4 - s_1)}{T_H(s_4 - s_1)} = 1 - \frac{T_L}{T_H}$$

Practical Problems

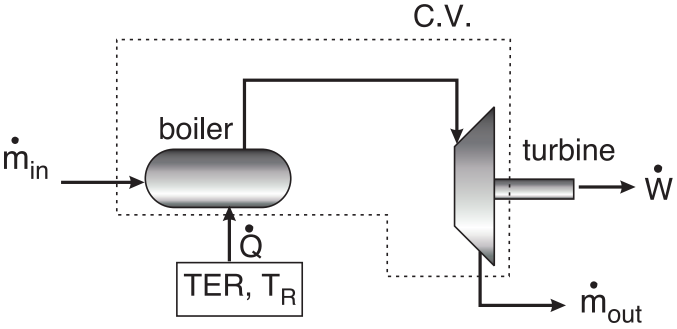
- at state point 1 the steam is wet at T_L and it is difficult to pump water/steam (two phase) to state point 2
- the pump can be sized smaller if the fluid is 100% liquid water
- the pump is smaller, cheaper and more efficient
- can we devise a Carnot cycle to operate outside the wet vapor region



  - between state points 2 and 3 the vapor must be isothermal and at different pressures - this is difficult to achieve
  - the high temperature and pressure at 2 and 3 present metallurgical limitations

The net effect is that the Carnot cycle is <u>not</u> feasible for steam power plants.

Example: A steady flow process



Find: $\dot{W}_{max} = ?$

Solution:

Assume S.S.S.F and $\Delta PE = 0$, $\Delta KE = 0$

From the 1st law we know

$$\left(\frac{d\cancel{E}^{\nearrow 0}}{dt}\right)_{CV} = \dot{Q} - \dot{W} + (\dot{m}h)_{in} - (\dot{m}h)_{out}$$

From the 2nd law we know

$$\left(\frac{d\cancel{S}^{\nearrow 0}}{dt}\right)_{CV} = \left(\dot{m}s + \frac{\dot{Q}}{T_R}\right)_{in} - (\dot{m}s)_{out} + \dot{S}_{gen}$$

Rearranging the 2nd law to isolate $\dot{Q}$

$$\dot{Q} = (\dot{m}s)_{out}\, T_R - (\dot{m}s)_{in}\, T_R - \dot{S}_{gen} T_R$$

Then substituting this into the 1st law

$$\dot{W} = \left\{ \underbrace{\dot{m}[h - T_R s]_{in}}_{b_{in}} - \underbrace{\dot{m}[h - T_R s]_{out}}_{b_{out}} \right\} - T_R \dot{S}_{gen}$$

Therefore we can write

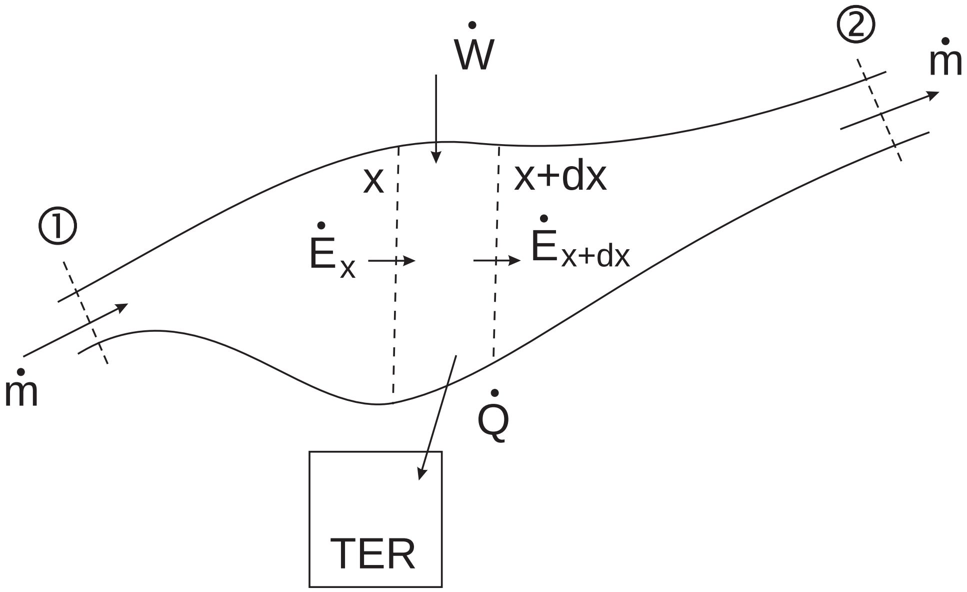
$$\dot{W} \le \dot{m}(b_{in} - b_{out})$$

where for a reversible process with $\dot{S}_{gen} = 0$ we can write

$$\dot{W}_{max} = \dot{m}(b_{in} - b_{out})$$

Aside: $b = h - T_R s$ is referred to as the availability and is a measure of the “available energy” after the energy destroyed as a result of irreversibilities is removed.

Steady State, Steady Flow in a Flow Channel of Arbitrary Cross-section with Work and Heat Transfer



$$\begin{aligned} d\dot{E} &= \dot{E}_{final} - \dot{E}_{initial} \\ &= \dot{E}_{x+dx} - \dot{E}_x \end{aligned}$$

where

$$\begin{aligned} \dot{E} &= \dot{m}(e + Pv) \\ &= \dot{m}\left(u + \frac{\mathcal{V}^2}{2} + gz + Pv\right) \end{aligned}$$

From the 1st law

$$\begin{matrix} rate\ of\ energy \\ storage \end{matrix} = \begin{matrix} rate\ of \\ work \end{matrix} + \begin{matrix} rate\ of \\ heat\ transfer \end{matrix} + \begin{matrix} net\ rate\ of\ energy \\ leaving\ the\ system \end{matrix}$$

$$\frac{dE_{CV}}{dt} = \delta\dot{W} - \delta\dot{Q} - \delta\dot{E} \qquad (1)$$

where $\frac{dE_{CV}}{dt} = 0$ for steady state.

Equation (1) becomes

$$0 = \delta\dot{W} - \delta\dot{Q} - \dot{m}\,\delta\left[u + Pv + \frac{\mathcal{V}^2}{2} + gz\right] \qquad (2)$$

From the 2nd law

$$\begin{matrix} rate\ of \\ entropy \\ storage \end{matrix} = \left\{ \begin{matrix} rate\ of \\ entropy \\ inflow \end{matrix} - \begin{matrix} rate\ of \\ entropy \\ outflow \end{matrix} \right\} + \begin{matrix} rate\ of \\ entropy \\ production \end{matrix}$$

$$\frac{dS_{CV}}{dt} = [\dot{m}s]_x - [\dot{m}s]_{x+dx} - \frac{\delta\dot{Q}}{T_{TER}} + \dot{S}_{gen}$$

where $\frac{dS_{CV}}{dt} = 0$ for steady state.

$$0 = -\dot{m}ds - \frac{\delta\dot{Q}}{T_{TER}} + \dot{S}_{gen}$$

or

$$\delta\dot{Q} = T_{TER}\,\dot{S}_{gen} - T_{TER}\,\dot{m}\,ds \qquad (3)$$

Combining (2) and (3) through $\delta\dot{Q}$

$$\boxed{T_{TER}\,\dot{S}_{gen} - T_{TER}\,\dot{m}\,ds = \delta\dot{W} - \dot{m}\,\delta\left(u + Pv + \frac{\mathcal{V}^2}{2} + gz\right)} \qquad (4)$$

Equation (4) can be used for any SS-SF process.

Special Cases

Reversible, SS-SF Process

Reversible implies ⇒ $\dot{S}_{gen} = 0$

- frictionless process
- heat transfer is allowed but must be across $\Delta T \rightarrow 0$
- which means $T_{TER} \approx T_{CV} = T$

Equation 4 becomes

$$\frac{\delta \dot{W}}{\dot{m}} = -Tds + \underbrace{du + d(Pv)}_{=\underbrace{du + Pdv}_{=Tds} + \underbrace{vdP}} + \delta \left(\frac{\mathcal{V}^2}{2} \right) + \delta(gz) \qquad (5)$$

Therefore

$$\frac{d\dot{W}}{\dot{m}} = vdP + d\left(\frac{\mathcal{V}^2}{2} \right) + d(gz) \qquad (6)$$

Integrating Eq. (6) between the inlet and the outlet

$$\frac{\dot{W}}{\dot{m}} = \int_{in}^{out} vdP + \underbrace{\left. \frac{\mathcal{V}^2}{2} \right|_{in}^{out}}_{\Delta KE} + \underbrace{\left. gz \right|_{in}^{out}}_{\Delta PE} \qquad (7)$$

but ΔKE and ΔPE are usually negligible.

If $\Delta KE + \Delta PE = 0$

$$\boxed{\frac{\dot{W}}{\dot{m}} = \int_{in}^{out} vdP} \qquad (8)$$

Equation can be used for a reversible, SS-SF flow in a liquid or a gas.

If we keep in mind

$$\rho_{liq} >> \rho_{gas} \quad \Rightarrow \quad v_{liq} << v_{gas}$$

i.e. water @ $25\ ^\circ C \ \ \rho = 997\ kg/m^3$ and air @ $25\ ^\circ C \ \ \rho = 1.18\ kg/m^3$

Therefore

$$\left(\frac{\dot{W}}{\dot{m}}\right)_{liq} << \left(\frac{\dot{W}}{\dot{m}}\right)_{gas}$$

For example: the work required to operate a pump is much less that that required to operate a compressor.

Incompressible Substance

This is a special case of Eq. (8) where $v = constant = v_{in} - v_{out}$.

From Equation (8)

$$\frac{\dot{W}}{\dot{m}} = v_{in}(P_{out} - P_{in}) \qquad (9)$$

The work term represents the minimum work required to pump a liquid from P_{in} to P_{out} with negligible ΔKE and ΔPE.

Incompressible Substance and $\delta\dot{W} = 0$

From Eq. (6)

$$vdP + \delta\left(\frac{\mathcal{V}^2}{2}\right) + \delta(gz) = 0 \qquad (10)$$

Therefore

$$d\left(\frac{P}{\rho}\right) + d\left(\frac{\mathcal{V}^2}{2}\right) + d(gz) = 0$$

$$d\left(\frac{P}{\rho} + \frac{\mathcal{V}^2}{2} + gz\right) = 0 \qquad (11)$$

Integrating gives

$$\frac{P}{\rho} + \frac{\mathcal{V}^2}{2} + gz = constant \qquad (12)$$

Equation (12) is Bernoulli's equation for frictionless flow with constant density. The constant is Bernoulli's constant, which remains constant along a streamline for steady, frictionless, incompressible flow.

Isothermal Ideal Gas, Compression/Expansion

This is a special case of Eq. (8) for an ideal gas where $Pv = RT$

$$Pv = constant = (Pv)_{in} = (Pv)_{out}$$

$$\frac{\dot{W}}{\dot{m}} = \int_{in}^{out} v dP = \int_{in}^{out} (Pv)_{in} \frac{dP}{P}$$

Therefore

$$\boxed{\frac{\dot{W}}{\dot{m}} = P_{in} v_{in} \ln\left(\frac{P_{out}}{P_{in}}\right)} \qquad (13)$$

Isentropic Ideal Gas, Compression/Expansion

Isentropic implies a reversible and adiabatic process where $s = constant$. With an ideal gas, $Pv^k = constant$ and $(Pv^k)_{in} = (Pv^k)_{out}$.

Equation (8) becomes

$$\frac{\dot{W}}{\dot{m}} = \int_{in}^{out} v dP = \int_{in}^{out} \left[\frac{(Pv^k)_{in}}{P}\right]^{1/k} dP$$

$$\boxed{\frac{\dot{W}}{\dot{m}} = \left(\frac{k}{k-1}\right)(Pv)_{in}\left[\left(\frac{P_{out}}{P_{in}}\right)^{(k-1)/k} - 1\right] = C_p(T_{out} - T_{in})} \qquad (14)$$

The right side of Eq. (14) is based on the fact that $\Delta KE + \Delta PE = 0$ and $dh = du + dPv$ and $du = 0$. Which leads to $h = \int vdP$.

Note: for the same inlet state and pressure ratio

$$\Rightarrow \left(\frac{\dot{W}}{\dot{m}}\right)_{rev.,isothermal} < \left(\frac{\dot{W}}{\dot{m}}\right)_{rev.,adiabatic}$$