

Sustainable Energy Transformation Technologies, SH2706

Lecture No 6

Title:

Work extraction constraints: entropy and exergy

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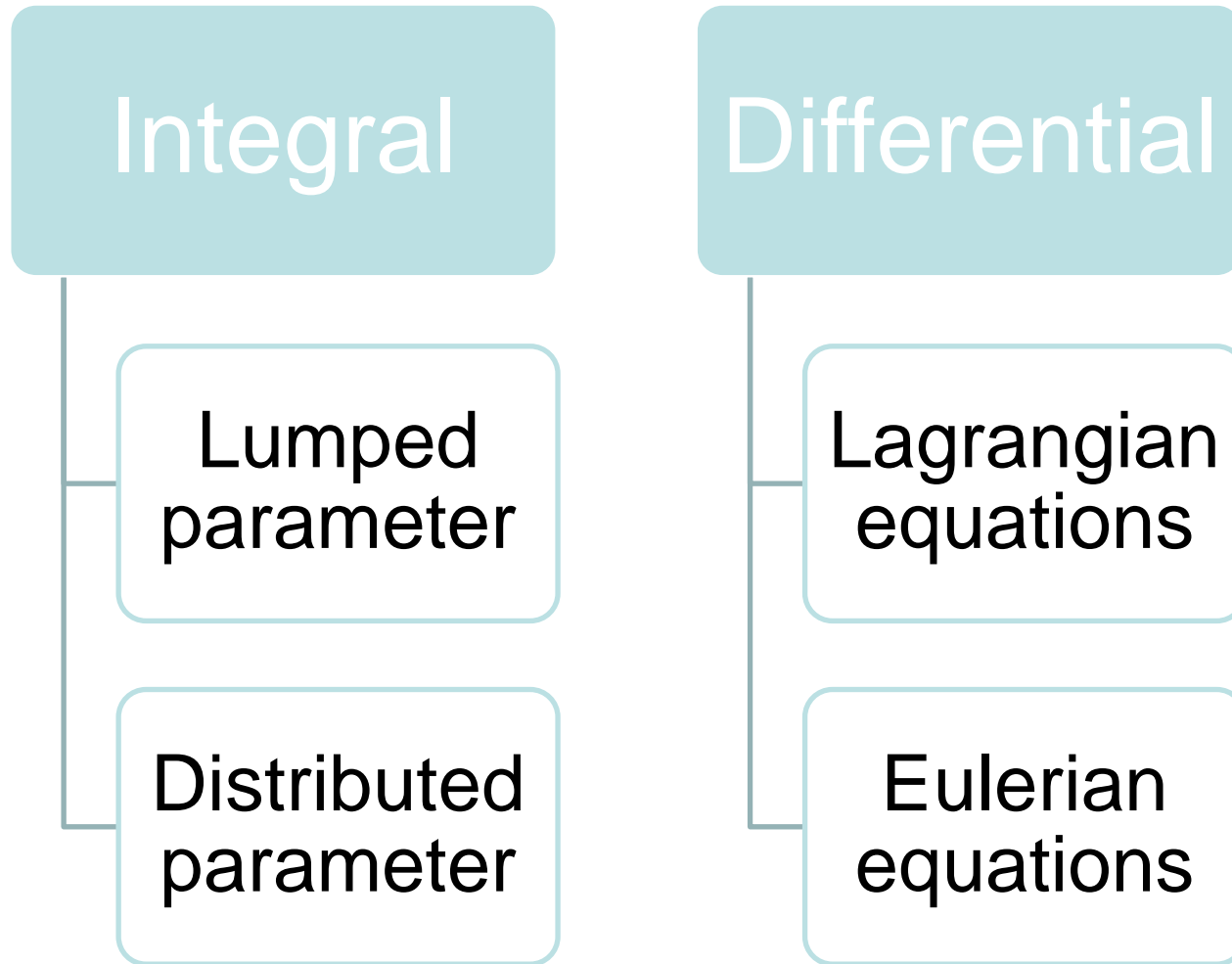
Outline

- Introduction
- Balance equations using lumped parameter approach
 - control mass formulation
 - control volume formulation
- Entropy analysis
- Exergy analysis

Introduction

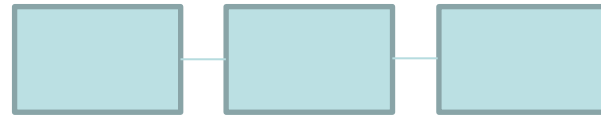
- Thermal analyses of energy transformation systems involve solution of conservation (balance) equations
- Primarily, **conservation of mass, momentum and energy** is considered
- Often these equations are referred to as **transport equations**
- The thermal analyses allow to determine the distributions of **temperature, pressure and flows in the system**

Types of Transport Equations



Integral Approach

- The integral approach is suitable for an analysis of the behaviour of a specific mass or region of a system as a whole



System of three connected volumes

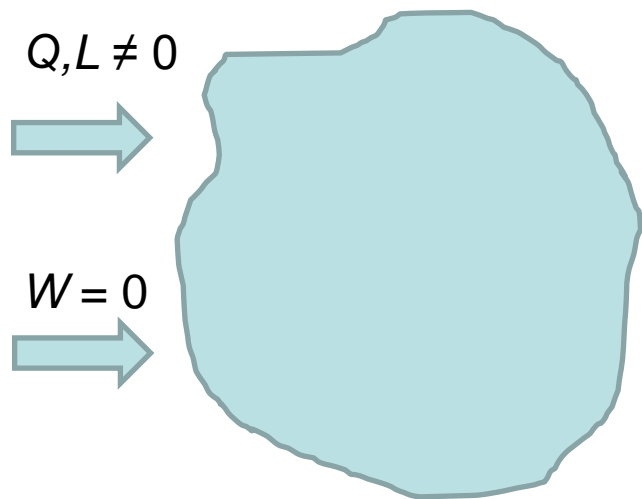
- It can be divided as:
 - **lumped parameter integral approach**, when the medium is present in several sections (volumes), and within each section the spatial distributions of variables and material properties are ignored
 - **distributed parameter integral approach**, in which the spatial distributions of variables and material properties are taken into account

Differential Approach

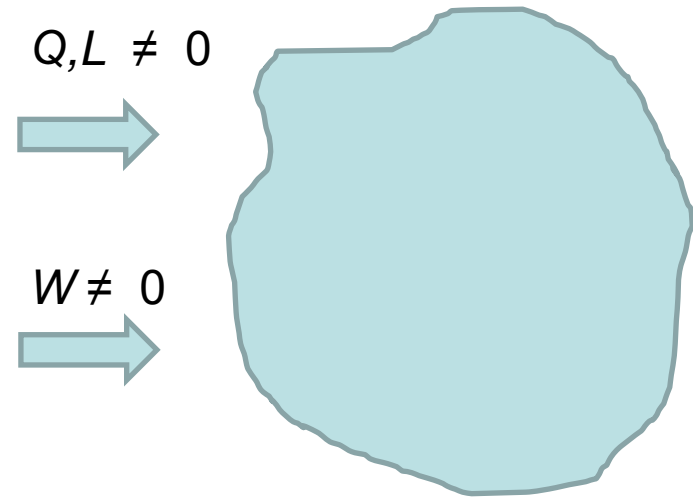
- The differential approach is a distributed parameter approach where the balance equations are formulated for each point and not for the entire system
- It can be divided into two categories:
 - **Lagrangian approach**, when the coordinates move at the local medium velocity
 - **Eulerian approach**, when the coordinates are moving at any velocity, and in particular, they can be stationary in space at a particular position
- Further in this lecture we discuss lumped parameter approach only

Control Mass and Control Volume

- Lumped parameter approach can be applied in two types of systems:
 - control mass system (or closed system)
 - control volume system (or open system)



Control Mass system



Control Volume system

Control Mass Formulation (1)

- Control mass (CM) system is defined as such a system that no mass crosses its boundary
- A boundary which is not crossed by mass is called a **material boundary** and the corresponding volume: a **material volume**
- Mass conservation for such system is just stating that the mass (m) in the system (material) volume (V_m) is constant

$$\frac{Dm}{Dt} = 0$$

- Here D/Dt is the material (or substantial) derivative $\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla$

Control Mass Formulation (2)

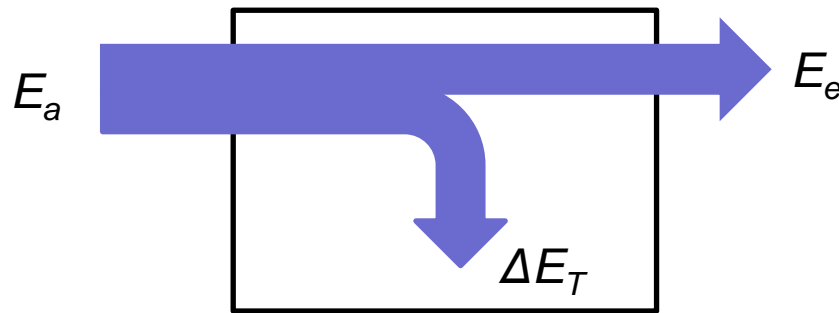
- The rate of momentum creation of the CM system is equal to the net external force (Newton's second law)

$$\frac{D(m\mathbf{v})}{Dt} = \frac{D\mathbf{p}}{Dt} = \sum_k \mathbf{F}_k$$

- Here $\mathbf{p} = m\mathbf{v}$ is the system momentum and \mathbf{F}_k is the k -th external force acting on the system

Control Mass Formulation (3)

- The energy conservation (first law) states that the rate of change of the stored energy in CM is equal to the difference between the rate of energy addition (as heat or work) to CM and the rate of energy extraction from CM



Since no substance passes through the boundary, energy transfer can take place only through heat (Q) and work (L):

$$\Delta E_T = Q - L$$

By convention, heat added to a system and work extracted from a system are considered positive

E_a – energy added; E_e – energy extracted; ΔE_T – system total energy change;

Control Mass Formulation (4)

- The total energy of the system can be defined as a sum of the internal energy (E_I), kinetic energy (E_K) and potential energy (E_P):

$$E_T = E_I + E_K + E_P$$

- The kinetic and the potential energies are related to the macroscopic effects of the system as a whole
- The internal energy is entirely resulting from microscopic effects:
 - oscillatory, translational and rotational kinetic energy of atoms and molecules; potential energy in the field of attraction forces between molecules; chemical energy related to a possibility of reconstruction of molecules; nuclear energy

Control Mass Formulation (5)

- The total work can be partitioned into a shaft work L_{shaft} (positive in a turbine and negative in a pump), work transmitted through a control boundary by normal (L_{normal}) and tangential (L_{shear}) forces:

$$L = L_{shaft} + L_{normal} + L_{shear}$$

- Thus the energy equation for a control mass system is

$$\Delta E_T = Q - L_{shaft} - L_{normal} - L_{shear}$$

Control Mass Formulation (6)

- Typically energy transformation systems operate continuously, and the energy conservation equation can be expressed in the time rate:

$$\frac{dE_T}{dt} = \frac{\delta Q}{dt} - \frac{\delta L_{shaft}}{dt} - \frac{\delta L_{normal}}{dt} - \frac{\delta L_{shear}}{dt}$$

- Using notation $q = \delta Q/dt$ (thermal power) and $N = \delta L/dt$ (mechanical power), we have

$$\frac{dE_T}{dt} = q - N_{shaft} - N_{normal} - N_{shear}$$

Control Mass Formulation (7)

- Frequently the energy equation is expressed in terms of the specific total energy, that is the total energy per unit mass, $e_T = E_T/m$, where $e_T = e_I + e_K + e_P$:

$$\frac{dE_T}{dt} = \frac{d}{dt} \left[m(e_I + e_K + e_P) \right] = q - N_{shaft} - N_{normal} - N_{shear}$$

- we should note that e_I is the specific internal energy, $e_K = U^2/2$ – is the specific kinetic energy and $e_P = gh$ – is the specific potential energy

Control Mass Formulation (8)

- The entropy inequality (the second law) states that the net change of the entropy of CM interacting with its surroundings and the entropy change of the surroundings of CM should be equal to or greater than zero
- Since no mass is crossing CM boundary, the entropy exchanges with the surroundings are associated with heat interactions
- The entropy inequality is then

$$\frac{DS}{Dt} = \left(\frac{dS}{dt} \right)_{CM} \geq \frac{(\delta Q/dt)_{CM}}{T_S} \quad T_S - \text{temperature at the location where } \delta Q \text{ is supplied}$$

Control Mass Formulation (9)

- For irreversible (real-life) processes the inequality holds, since additional entropy is generated in CM due to irreversibility. Then we have:

$$\left(\frac{dS}{dt} \right)_{CM} = \dot{S}_{gen} + \frac{(\delta Q/dt)_{CM}}{T_S}$$

- here \dot{S}_{gen} is the rate of entropy generation due to irreversibility

Control Mass Formulation (10)

- An immediate consequence of the entropy balance equation is that for a reversible adiabatic process the entropy of the control mass system is unchanged

$$\left(\frac{dS}{dt} \right)_{CM} = \dot{S}_{gen} + \frac{\left(\overset{=0}{\delta Q / dt} \right)_{CM}}{T_s} = 0$$

- Such process is also termed as an **isentropic process**

Control Volume Formulation (1)

- Control volume (CV) system is defined as such a system that both mass and heat can cross its boundary
- Mass conservation for such system is stating that the net mass flow rate into the system volume (V_{CV}) equals the rate of change of the mass in the volume

$$\frac{Dm}{Dt} = \left(\frac{dm}{dt} \right)_{CV} - \sum_i W_i = 0 \quad \text{or} \quad \left(\frac{dm}{dt} \right)_{CV} = \sum_i W_i$$

- Here W_i is a mass flow rate through port i and $(dm/dt)_{CV}$ is the rate of mass change in the control volume
- Note that $W > 0$ for mass flow into the volume

Control Volume Formulation (2)

- The rate of momentum creation of the system is equal to the net external force and the net influx of momentum to the system (Newton's second law)

$$\underbrace{\left[\frac{d(m\mathbf{v})}{dt} \right]_{CV}}_{\text{momentum rate-of-change}} = \underbrace{\sum_i W_i \mathbf{v}_i}_{\text{net influx of momentum}} + \underbrace{\sum_k \mathbf{F}_k}_{\text{net external force}}$$

Control Volume Formulation (3)

- The energy conservation (first law) applied to a control volume states that the rate of change of the stored energy in CV is equal to the net rate of energy influx to CV and any sources or sinks within the volume
- Let us assume that substance with mass dm and the total specific energy $e_T = e_I + e_K + e_P$ enters the control volume, in which the prevailing pressure is p
- Since mass dm has a volume $dV = dm/\rho$ (ρ – density) this process requires additional work to be performed against the system pressure equal to $\delta L_m = -pdV = -pdm/\rho$

Control Volume Formulation (4)

- Thus the total energy change of the system is

$$\frac{dE_T}{dt} = e_T W - (-pW / \rho) = (e_T + p / \rho) W = W (e_I + p / \rho + e_K + e_P)$$

- since the specific enthalpy is $i = e_I + p / \rho$ we can write

$$\frac{dE_T}{dt} = W (i + e_K + e_P)$$

- and the energy conservation equation becomes

$$\frac{dE_T}{dt} = q - N_{shaft} - N_{normal} - N_{shear} + \sum_{j \in in} (i + e_P + e_K)_j W_j - \sum_{k \in out} (i + e_P + e_K)_k W_k$$

Importance of the Second Law

- Any analysis of Energy Transformation Systems (ETS) must include the Second Law of Thermodynamics
- This is not because the second law is necessary to determine the flow and temperature fields (for that purpose the first law is used)
- Second law helps to strive after systems with high thermodynamic efficiency, meaning **minimum generation of entropy**, or **minimum destruction of available work (exergy)**
- The second law quantifies the real-life fact that all processes are irreversible and supports the applied field of **entropy generation minimization**

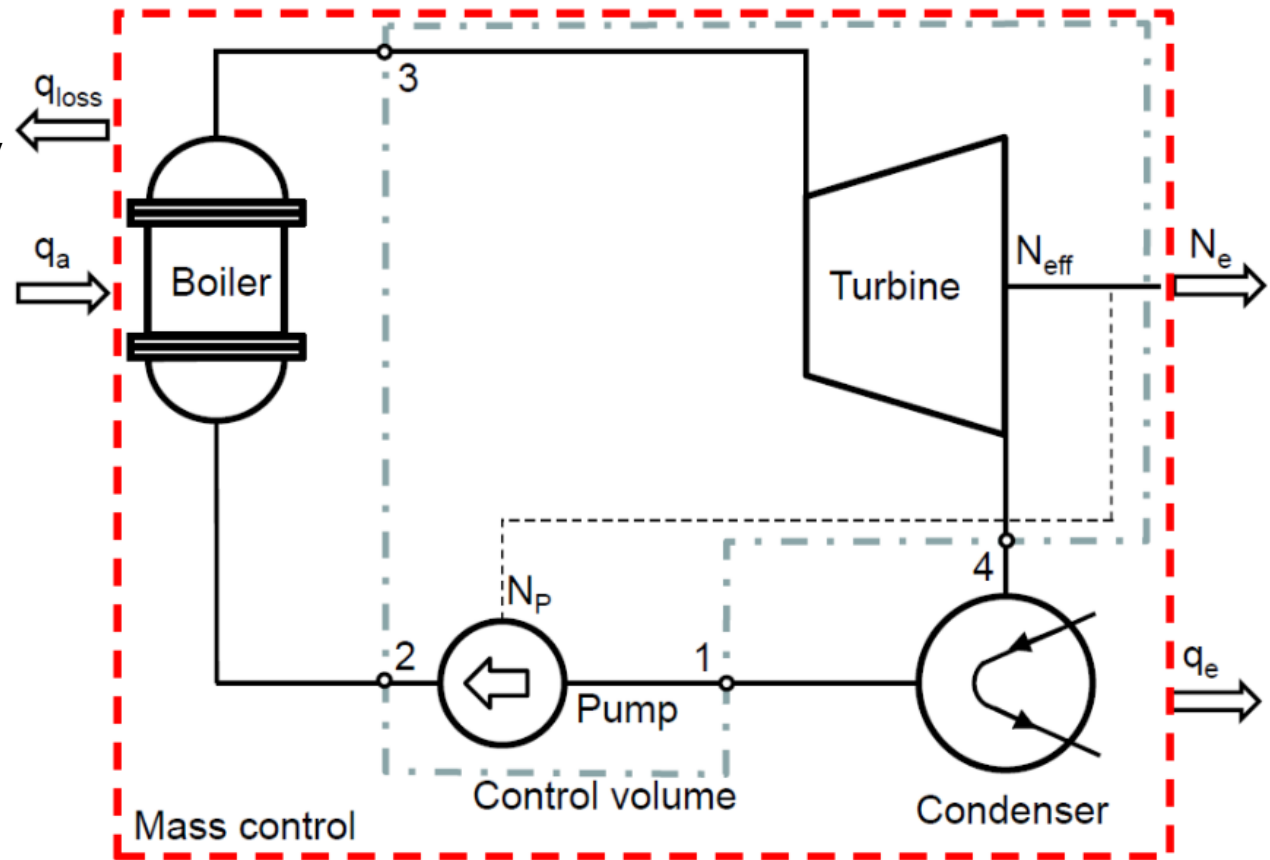
Entropy Analysis (1)

For system shown in the picture, we can write mass, energy and entropy balances.

For that purpose we will use the control volume as indicated in the picture.

The control volume has two inflow ports: (3) and (1) and two outflow ports: (2) and (4).

The mass, energy and entropy carried to the system through port 1 per unit time is \dot{W}_1 , $\dot{W}_1 i_1$, $\dot{W}_1 s_1$



The entropy decrease per unit time due to heat loss q_{loss} is $(dS/dt)_{\text{loss}}$ and entropy increase per unit time inside the control volume is $(dS/dt)_{\text{gen}}$

Entropy Analysis (2)

Mass conservation applied to the control volume gives:

$$W_3 - W_4 + W_1 - W_2 = 0$$

This equation is satisfied automatically since:

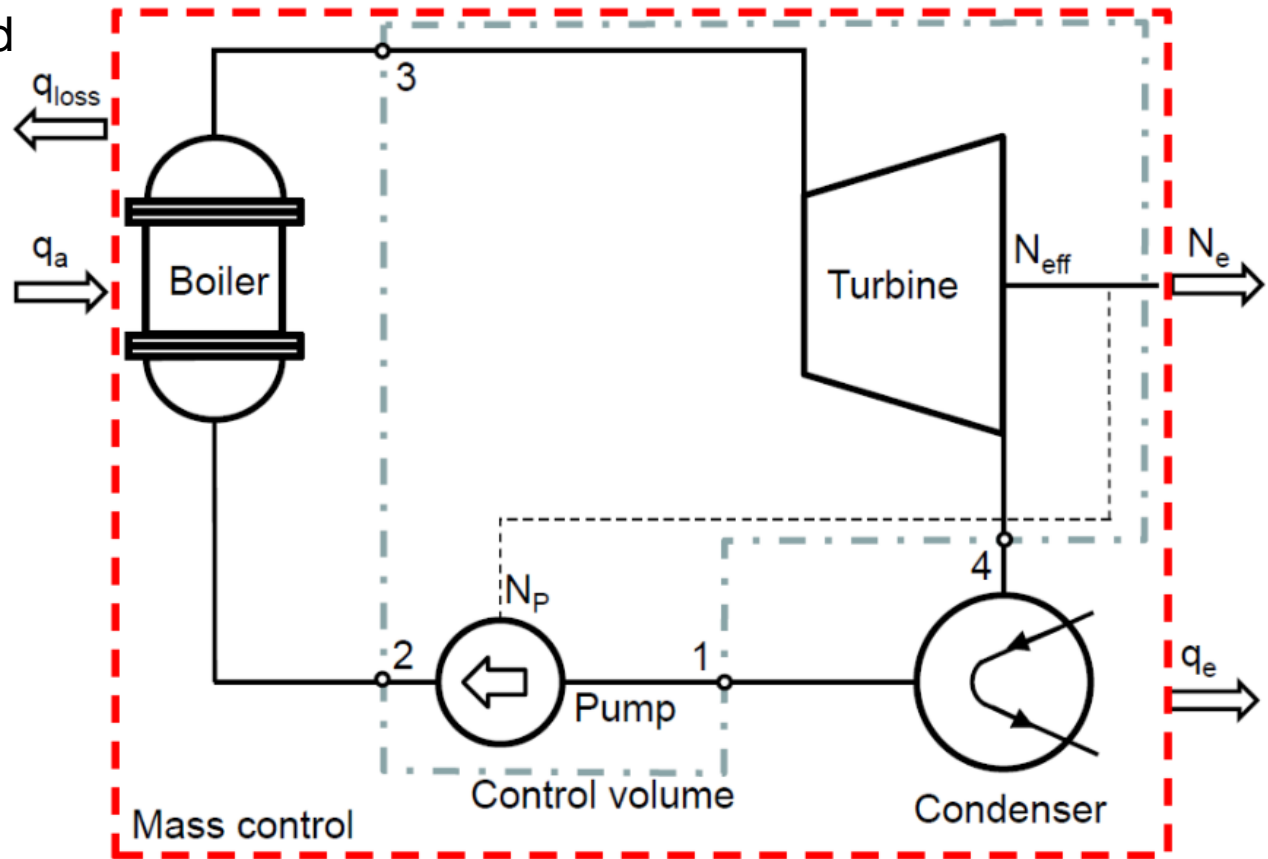
$$W_3 = W_4 = W_1 = W_2$$

Energy conservation gives:

$$q_a + q_{loss} + q_e - N_e = 0,$$

where $q_a = W_3 i_3 - W_2 i_2$ (added heat) and

$q_e = W_1 i_1 - W_4 i_4$ (extracted heat). $q_{loss} < 0$ represents systems' thermal losses



Entropy balance for the control volume reads:

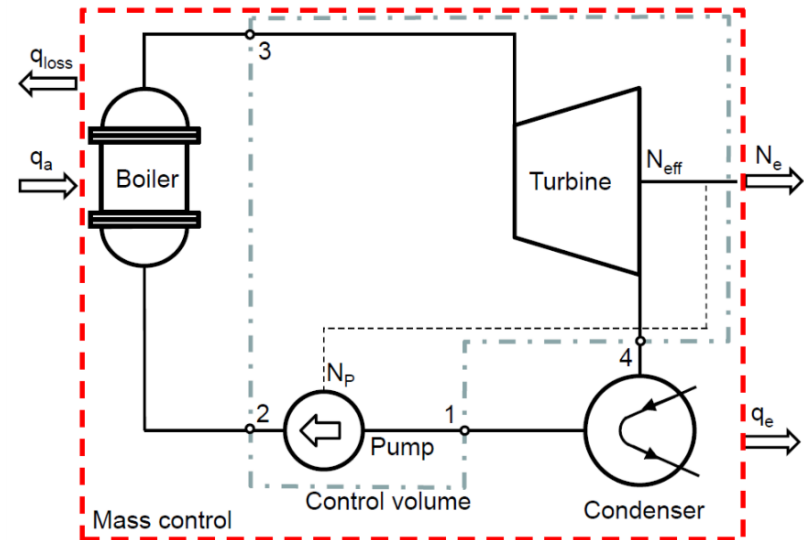
$$W_3 s_3 - W_2 s_2 + W_1 s_1 - W_4 s_4 + (dS/dt)_{loss} + (dS/dt)_{gen} = 0$$

Entropy Analysis (3)

(1) Thus, the following entropy balance is obtained:

$$W_b (s_3 - s_2) + W_c (s_1 - s_4) + \left(\frac{dS}{dt} \right)_{loss} + \left(\frac{dS}{dt} \right)_{gen} = 0$$

here we note that $W_3 = W_2 = W_b$ (flow through the boiler) and $W_4 = W_1 = W_c$ (flow through the condenser). At steady state operation they are equal: $W_b = W_c$.



(2) From the energy balance we have:

$$W_b (i_3 - i_2) = q_a \Rightarrow W_b = \frac{q_a}{(i_3 - i_2)}$$

$$W_c (i_1 - i_4) = q_e \Rightarrow W_c = \frac{q_e}{(i_1 - i_4)}$$

(3) Combining the energy and entropy equations yields:

$$q_a \frac{s_3 - s_2}{i_3 - i_2} + q_e \frac{s_1 - s_4}{i_1 - i_4} + \left(\frac{dS}{dt} \right)_{loss} + \left(\frac{dS}{dt} \right)_{gen} = 0$$

Entropy Analysis (4)

(1) Now the entropy balance is as follows:

$$q_a \frac{s_3 - s_2}{i_3 - i_2} + q_e \frac{s_1 - s_4}{i_1 - i_4} + \left(\frac{dS}{dt} \right)_{loss} + \left(\frac{dS}{dt} \right)_{gen} = 0$$

We define the **average thermodynamic temperature** for heat addition in the boiler as:

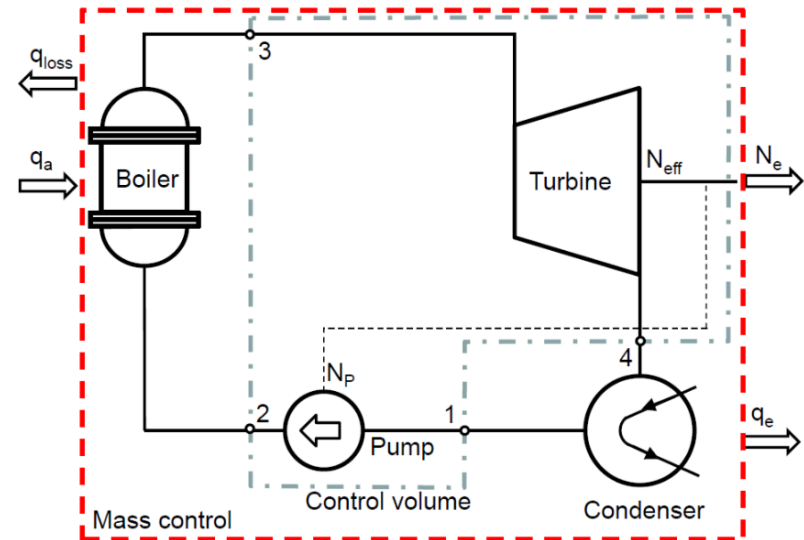
$$\bar{T}_a = \left| \frac{i_3 - i_2}{s_3 - s_2} \right|$$

and for heat extraction in the condenser as:

$$\bar{T}_e = \left| \frac{i_4 - i_1}{s_4 - s_1} \right|$$

(2) The entropy balance is now:

$$\frac{q_a}{\bar{T}_a} + \frac{q_e}{\bar{T}_e} + \left(\frac{dS}{dt} \right)_{loss} + \left(\frac{dS}{dt} \right)_{gen} = 0$$



(3) We repeat here the energy conservation:

$$q_a + q_e + q_{loss} - N_e = 0$$

or:

$$q_e = -q_a - q_{loss} + N_e$$

Entropy Analysis (5)

(1) We combine now the energy conservation equation with the entropy balance equation:

$$\frac{q_a}{\bar{T}_a} + \frac{q_e}{\bar{T}_e} + \left(\frac{dS}{dt} \right)_{loss} + \left(\frac{dS}{dt} \right)_{gen} = 0$$

$$q_e = -q_a - q_{loss} + N_e$$

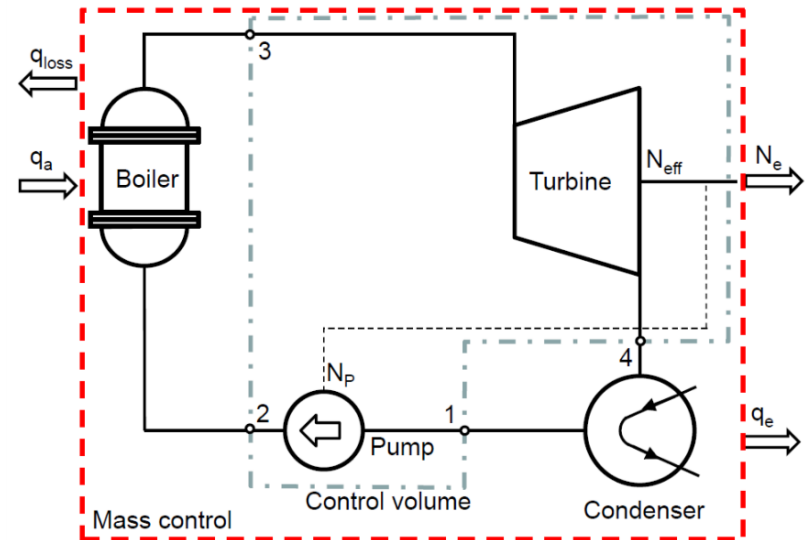
and we get:

$$\frac{q_a}{\bar{T}_a} - \frac{q_a}{\bar{T}_e} - \frac{q_{loss}}{\bar{T}_e} + \frac{N_e}{\bar{T}_e} + \left(\frac{dS}{dt} \right)_{loss} + \left(\frac{dS}{dt} \right)_{gen} = 0$$

This gives the following expression for the extracted power:

$$N_e = q_a \left(1 - \frac{\bar{T}_e}{\bar{T}_a} \right) + q_{loss} - \bar{T}_e \left(\frac{dS}{dt} \right)_{loss} - \bar{T}_e \left(\frac{dS}{dt} \right)_{gen}$$

note that
 $q_{loss} < 0$



Entropy Analysis (6)

We have obtained the following expression for the extracted power:

$$N_e =$$

$$q_a \left(1 - \frac{\bar{T}_e}{\bar{T}_a} \right)$$

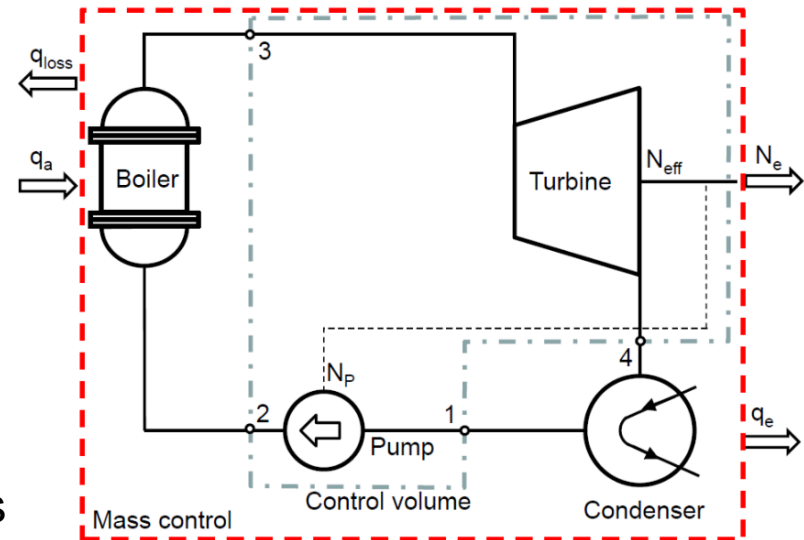
Carnot heat engine power

$$- \left[\bar{T}_e \left(\frac{dS}{dt} \right)_{loss} - q_{loss} \right]$$

Power loss due to heat loss

$$- \bar{T}_e \left(\frac{dS}{dt} \right)_{gen}$$

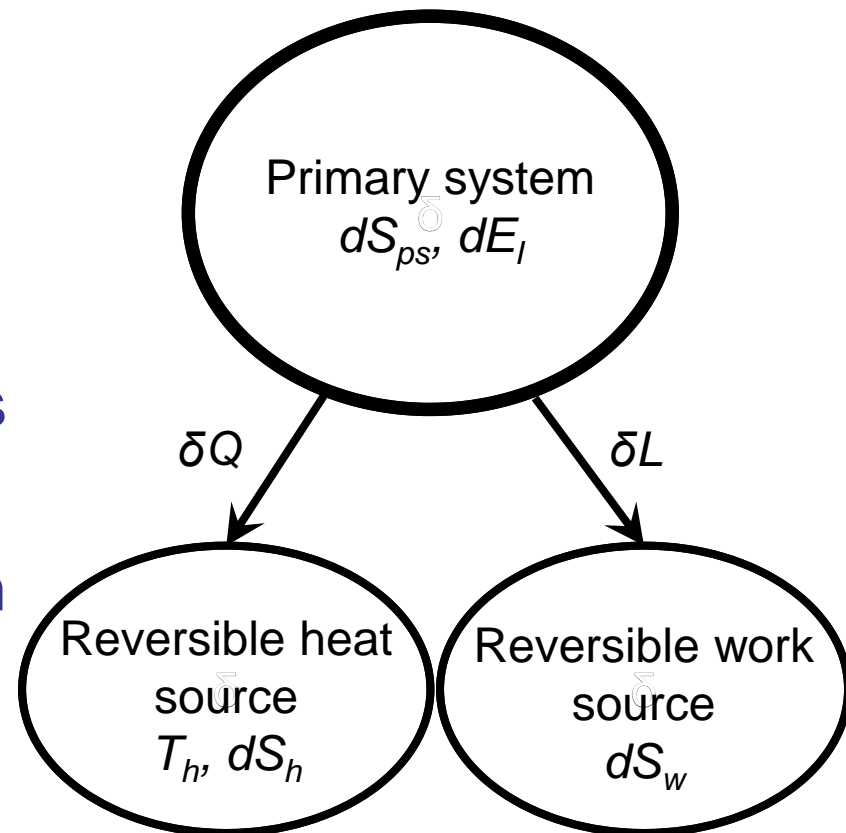
Power loss due to entropy generation



Since the two last terms on the right-hand side of the equation are negative, they all deteriorate the over-all system efficiency

Maximum Work (1)

- For a given finite thermodynamic cycle the maximum work can be determined from the first and second law of thermodynamics
- The derivation of the maximum work was first given by Gibbs who considered a **primary system** connected to **reversible heat** and **reversible work** sources



Maximum Work (2)

First law of thermodynamics for the primary system:

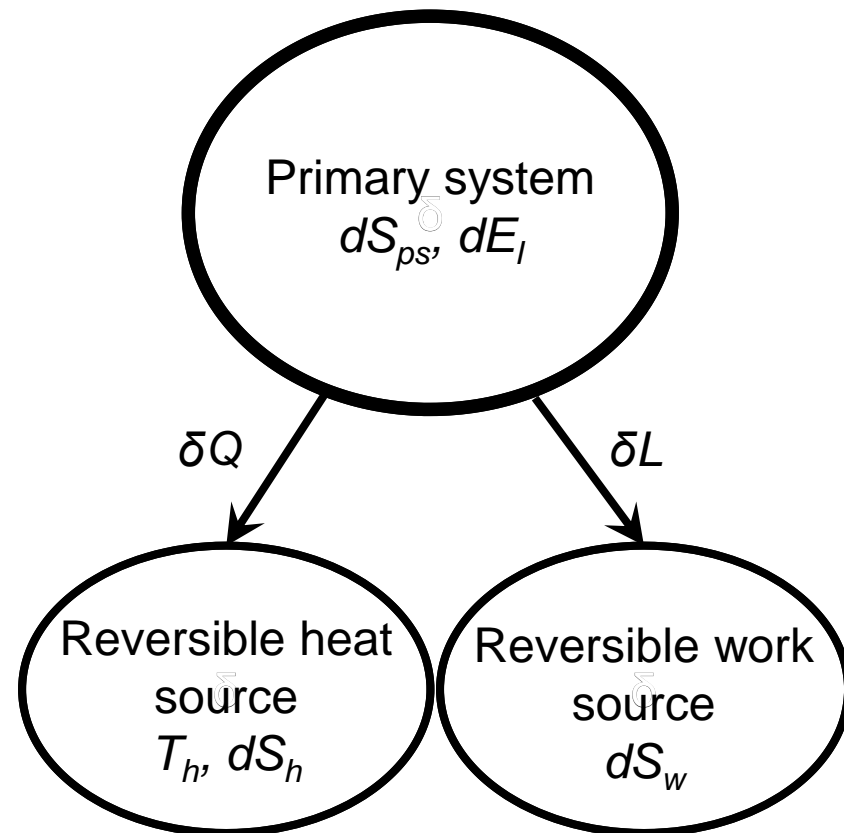
$$dE_I = \delta Q - \delta L$$

An internal energy change dE_I is equal to a heat exchanged with the RHS, δQ , minus a work exchanged with RWS, δL

Second law of thermodynamics says:

$$dS_h + dS_w + dS_{ps} \geq 0$$

The sum of entropy changes in the primary system and sources is non-negative



Maximum Work (3)

Reversibility of the work source dictates:

$$dS_w = 0$$

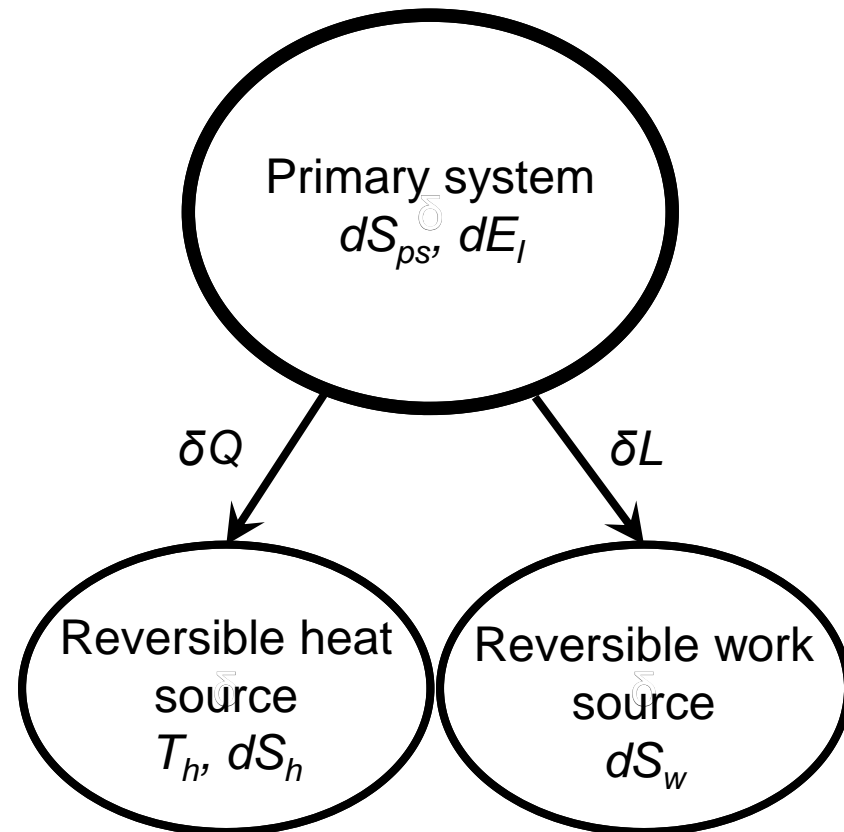
Reversibility of the heat source gives:

$$-\delta Q = T_h dS_h$$

Using the above in the 1st and 2nd law

gives
$$-\frac{dE_I + \delta L}{T_h} + dS_{ps} \geq 0$$

or
$$\delta L \leq T_h dS_{ps} - dE_I$$

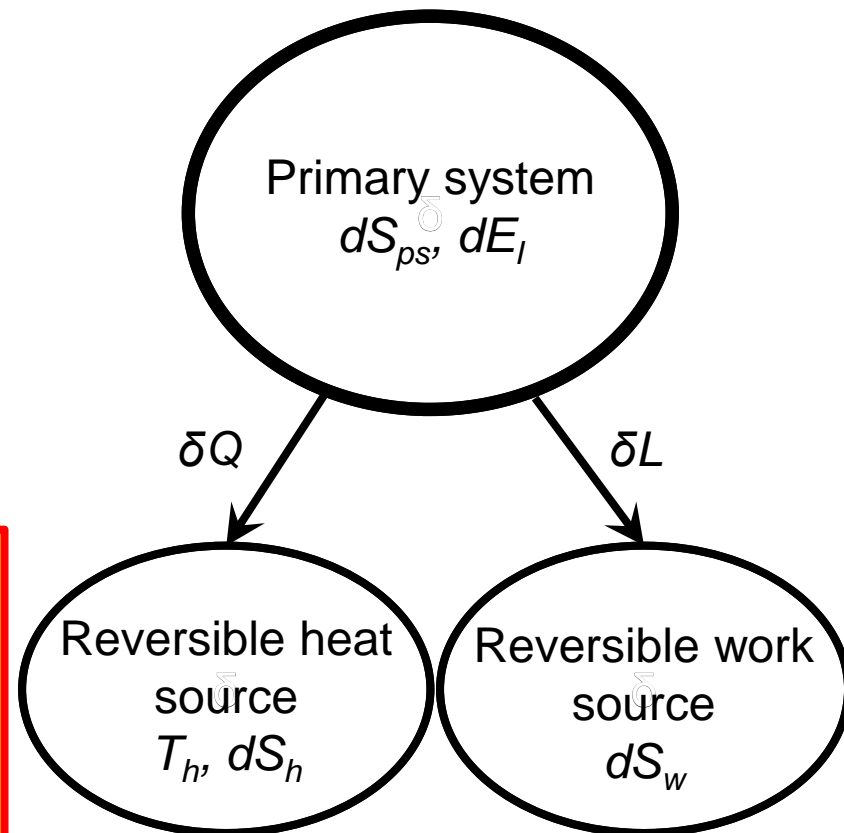


Maximum Work (4)

When the primary system is reversible the equality will hold and the work will be a maximum:

$$\delta L_{\max} = T_h dS_{ps} - dE_I$$

The above equation states that the maximum (positive) work can be obtained from a system whose internal energy drops (then $dE_I < 0$) reduced by $T_h dS_{ps}$ (note that $T_h dS_{ps} < 0$ when $\delta Q < 0$).



The maximum work principle gives explicit prove that it is not possible to use internal energy entirely to perform work. **The maximum work = internal energy drop reduced by $T_h dS_{ps}$, where $dS_{ps} < 0$, when $\delta Q < 0$**

Maximum Work (5)

- The derived maximum work principle is as follows:

$$\delta L_{\max} = T_h dS_{ps} - dE_I$$

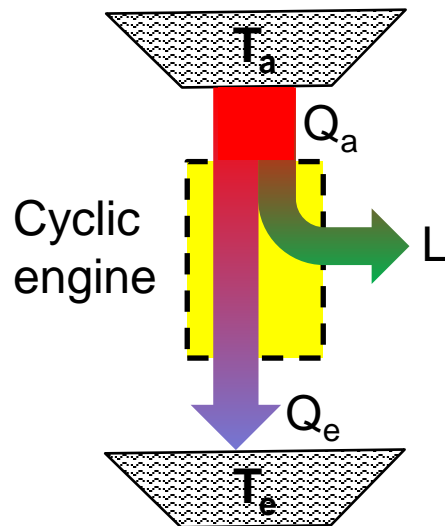
- We can integrate the above equations between two states (1) and (2) :

$$L_{\max} = \int_1^2 \delta L_{\max} = E_{I1} - E_{I2} - T_h (S_{ps1} - S_{ps2})$$

- It should be noted that this expression is not valid for cyclic processes where states (1) and (2) are identical

Maximum Work (6)

- To derive an expression for the maximum work in a cyclic process, we assume a model as follows:

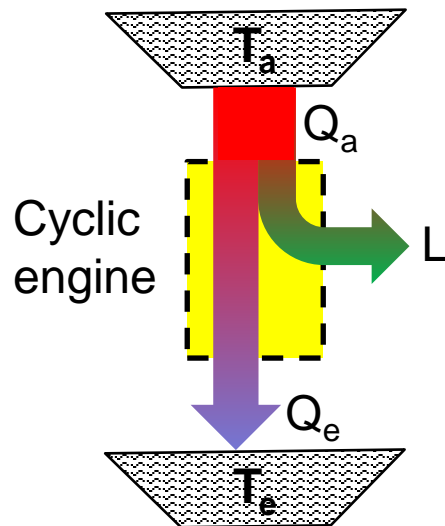


The engine operates between two heat reservoirs with temperatures T_a , from which, during a single cycle, heat Q_a is added to the system, and a reservoir with temperature T_e , to which heat Q_e , extracted from the system, is deposited. The engine delivers work L .

We will investigate what is the maximum work that can be delivered by the engine.

Maximum Work (7)

Note that from the point of view of the cyclic engine, $Q_a > 0$ (system gains heat), $L > 0$ (according to convention work delivered by a system is positive) and $Q_e < 0$ (system loses heat).



The first law for the engine operating during one cycle is as follows

$$\Delta E_I = Q_a + Q_e - L = 0$$

From which, we have:

$$L = Q_a + Q_e$$

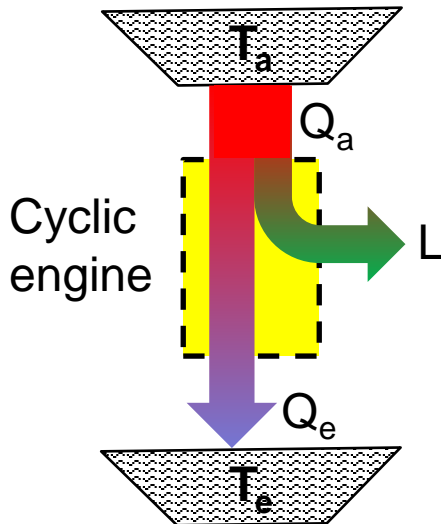
Maximum Work (8)

The reservoir with temperature T_a loses heat $Q_{Ra} = -Q_a < 0$ and its entropy changes as:

$$\Delta S_a = \frac{Q_{Ra}}{T_a} = -\frac{Q_a}{T_a} < 0$$

Accordingly, the entropy of the reservoir with temperature T_e changes as:

$$\Delta S_e = \frac{Q_{Re}}{T_e} = -\frac{Q_e}{T_a} > 0$$



Since the engine works in a cycle, the change of entropy for the engine itself is zero: $\Delta S_{Engine} = 0$

The total entropy change becomes: $\Delta S_{total} = \Delta S_a + \Delta S_e = \frac{Q_{Ra}}{T_a} + \frac{Q_{Re}}{T_e} > 0$

Maximum Work (9)

Summarizing:

From the 1st law we have:

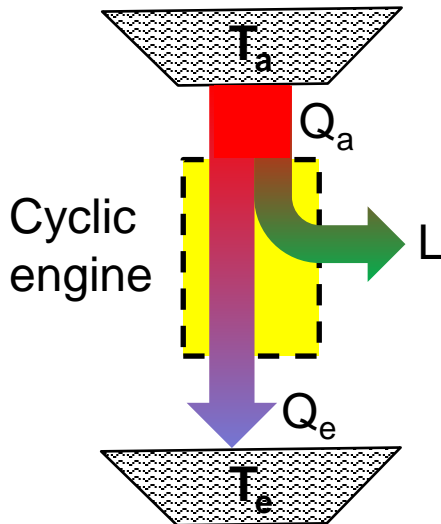
$$L = Q_a + Q_e$$

The 2nd law :

$$-\frac{Q_a}{T_a} - \frac{Q_e}{T_e} > 0$$

Combining the two expressions yields:

$$-\frac{Q_a}{T_a} - \frac{L - Q_a}{T_e} > 0 \quad \text{or} \quad Q_a \left(1 - \frac{T_e}{T_a} \right) - L > 0$$

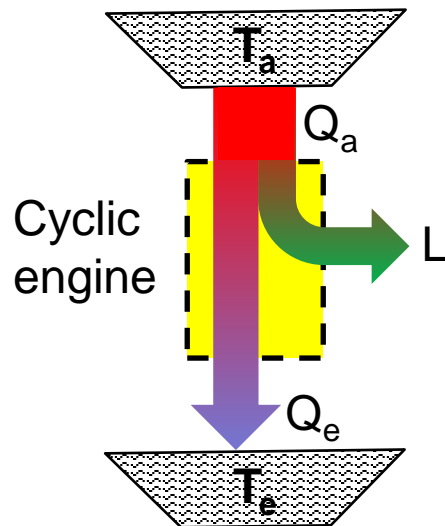


Maximum Work (10)

Thus for a cyclic engine the following limitation is valid :

$$L < Q_a \left(1 - \frac{T_e}{T_a} \right) = Q_a \eta_C \quad \text{where} \quad \eta_C \equiv \left(1 - \frac{T_e}{T_a} \right)$$

The obtained result indicates that only a fraction of the heat added to a cyclic engine can be converted into work.



The maximum work in a cyclic engine is thus:

$$L_{\max} = Q_a \eta_C$$

where η_C is the Carnot cycle efficiency

Exergy (1)

- Deriving the expression for the maximum work we noticed that only a fraction of the system energy is available (has potential) to do useful work
- Energy that is available to be used is called **exergy**, or sometime, available energy
- Determining exergy was the first goal of thermodynamics
- Application of exergy analyses in chemical plants was partially responsible for its huge grow in 20th century

Exergy (2)

- The fundamental difference between energy and exergy is that energy is conserved, whereas exergy is not
- From 1st law, energy input and output will always balance
- Exergy output will not balance the exergy input for real processes since a fraction of the exergy input will be destroyed according to the 2nd law

Exergy (3)

- An **energy efficiency** or **first law efficiency** will determine the most efficient process, where as little as possible of the input energy is wasted
- An **exergy efficiency** or **second law efficiency** will determine the most efficient process, where as little as possible of the available work, from a given input of available work, will be destroyed

Exergy (4)

- The thermal exergy B_{th} is defined as

$$B_{th} = \underbrace{E_I + p_0 V - T_0 S}_{\text{available physical energy}} - \underbrace{\sum_i \mu_{i0} n_i}_{\text{available chemical energy}}$$

internal energy
available pV work
entropic loss
available chemical energy

- For a mass stream penetrating a control volume boundary, it is convenient to partition the (total) exergy time rate \dot{B} as

$$\dot{B} = \underbrace{\dot{B}_k}_{\text{kinetic exergy}} + \underbrace{\dot{B}_p}_{\text{potential exergy}} + \underbrace{\dot{B}_{th}}_{\text{thermal exergy}} = W \left(\frac{U^2}{2} + gh + b_{th} \right)$$

- here U – absolute mean speed, h – center-of-mass elevation, b_{th} – specific thermal exergy

Exergy (5)

- Additionally, the thermal exergy is partitioned as

$$\dot{B}_{th} = \underbrace{\dot{B}_{ph}}_{\text{physical exergy}} + \underbrace{\dot{B}_{ch}}_{\text{chemical exergy}} = W(b_{ph} + b_{ch})$$

Chemical exergy only changes when chemical reactions take place (e.g. fuel combustion)

- where the physical exergy can be found as

$$\dot{B}_{ph} = Wb_{ph} = W(i_{ph} - T_0s_{ph}) = W[i - i_0 - T_0(s - s_0)]$$

- where i_{ph} , s_{ph} – specific physical enthalpy and entropy (calculated in reference to ambient), i_0 , s_0 – specific enthalpy and entropy at ambient pressure and temperature

Exergy (6)

- For an ideal gas, the specific physical exergy is obtained as

$$b_{ph} = c_p \left(T - T_0 - T_0 \ln \frac{T}{T_0} \right) + RT_0 \ln \frac{p}{p_0}$$

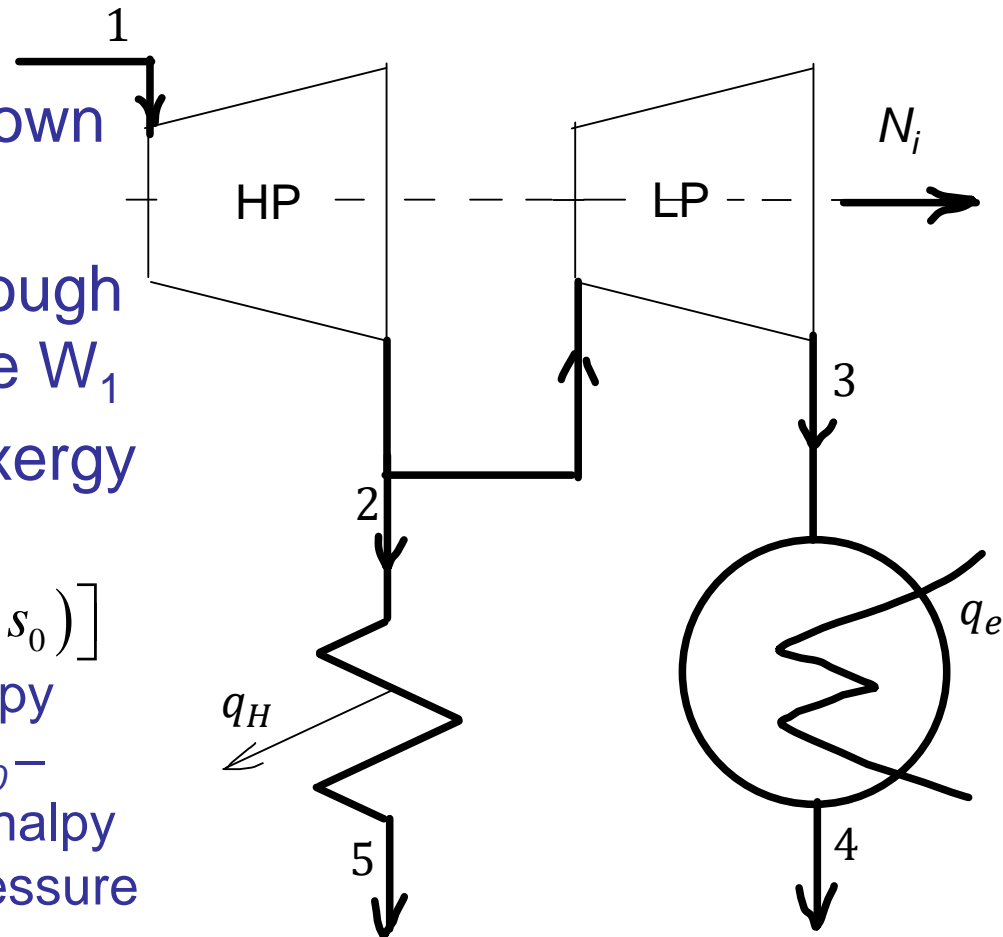
- where c_p is the specific heat at constant pressure, R is the specific gas constant, T , T_0 is the actual and ambient temperature and p , p_0 is the actual and ambient pressure

Exergy (7)

- Consider a system as shown in the figure
- Working fluid flows in through inlet 1 with mass flow rate W_1
- Thus the system gains exergy per unit time given as:

$$\dot{B}_1 = W_1 \left[i_1 - i_0 - T_0 (s_1 - s_0) \right]$$

- here i_1 , s_1 – specific enthalpy and entropy at inlet 1, i_0 , s_0 – working fluid's specific enthalpy and entropy at ambient pressure p_0 and temperature T_0 , respectively



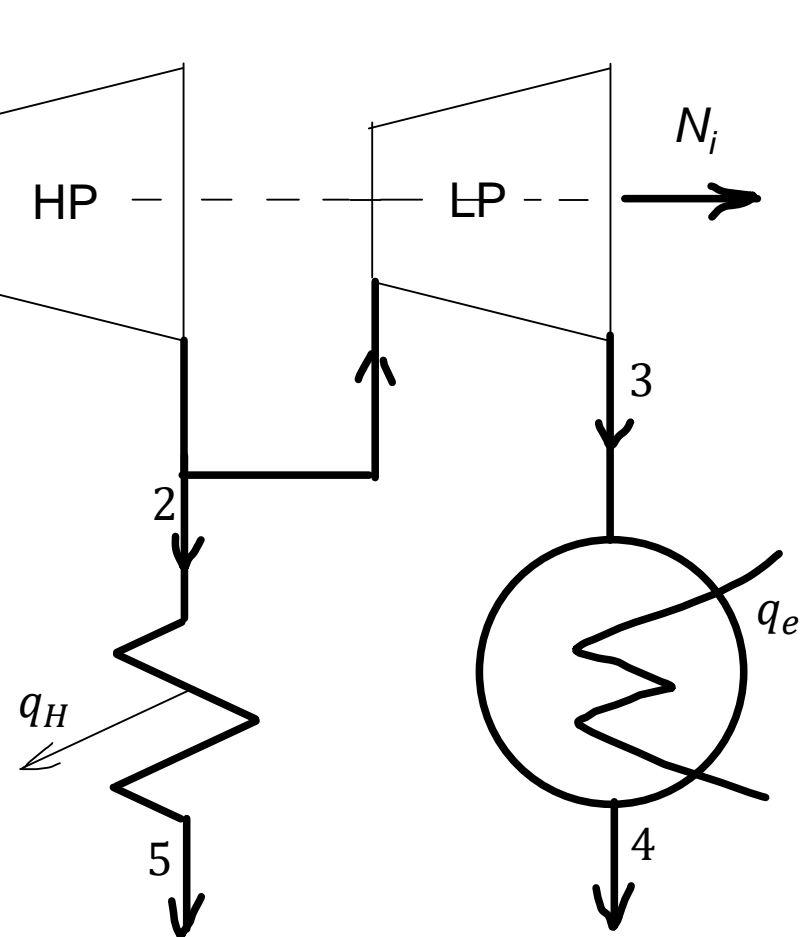
Exergy (8)

- Similarly, working fluid flows out through outlets 4 and 5 with mass flow rates W_4 and W_5 , respectively
- Thus the system loses exergy per unit time given as:

$$\dot{B}_4 = W_4 \left[i_4 - i_0 - T_0 (s_4 - s_0) \right]$$

$$\dot{B}_5 = W_5 \left[i_5 - i_0 - T_0 (s_5 - s_0) \right]$$

- here i_4 , s_4 – specific enthalpy and entropy at outlet 4, T_0 ambient temperature, etc

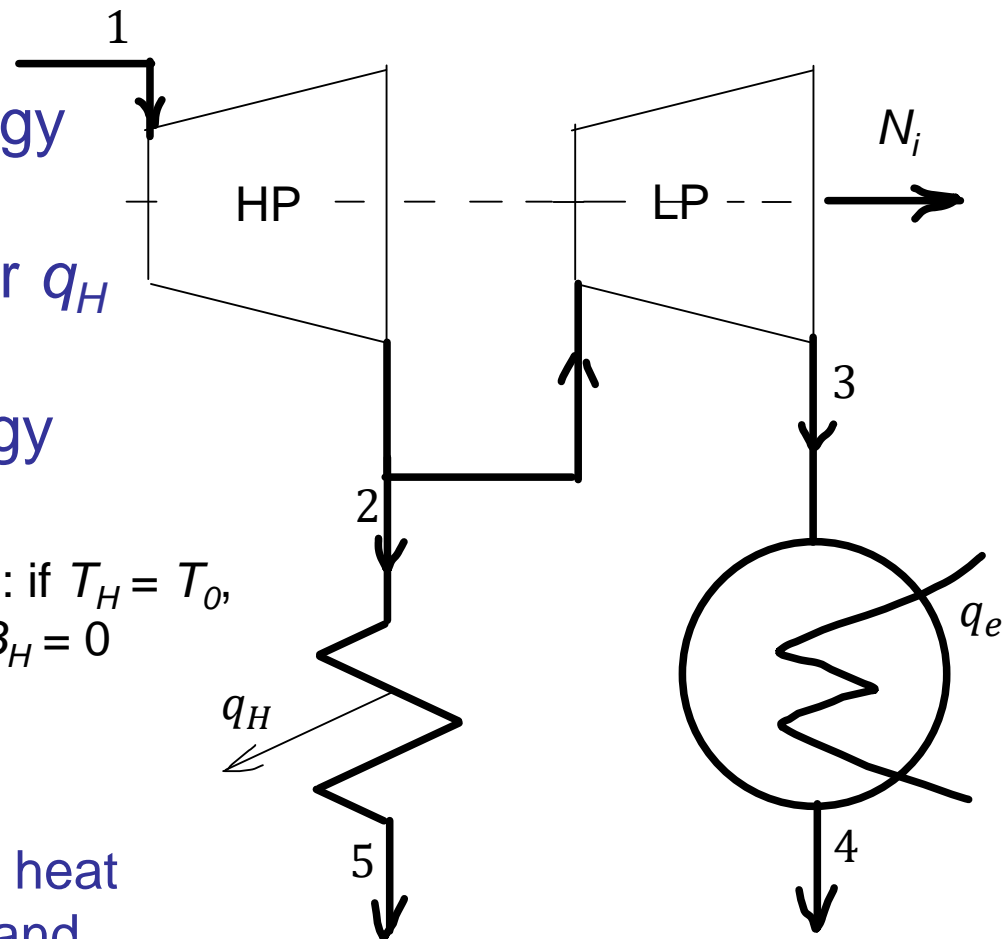


Exergy (9)

- There is also loss of exergy due to heat sinks. For example, if thermal power q_H is leaving the system at temperature T_H , the exergy loss is

$$\dot{B}_H = q_H \frac{T_H - T_0}{T_H} \quad \text{NOTE: if } T_H = T_0, \text{ then } B_H = 0$$

- Note that this exergy loss corresponds to the Carnot engine power working with heat q_H at high temperature T_H and low temperature T_0

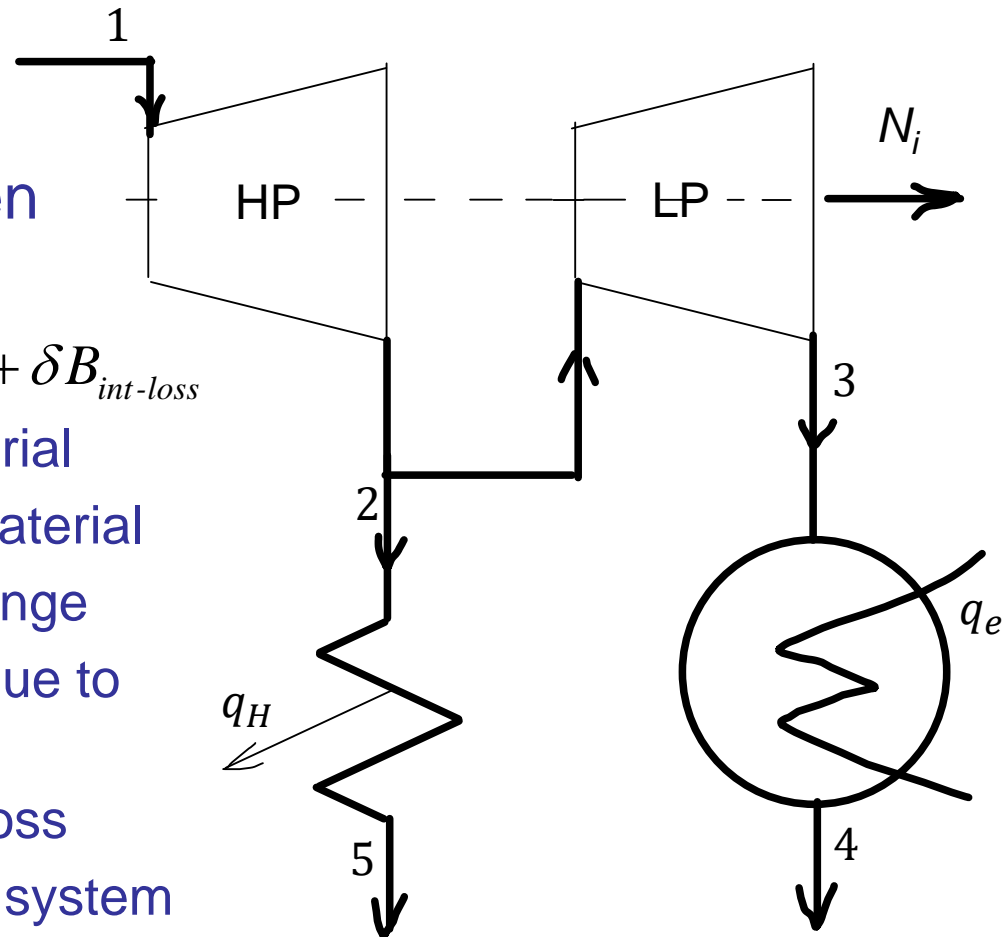


Exergy (10)

- The general rule for the exergy balance in an open system is as follows

$$B_a = \Delta B_{sys} + B_e + L + \Delta B_{sources} + \delta B_{int-loss}$$

- B_a – exergy of added material
- B_e – exergy of extracted material
- ΔB_{sys} – system exergy change
- ΔB_{source} – exergy change due to heat sources/sinks
- $\delta B_{int-loss}$ – internal exergy loss
- L – work performed by the system

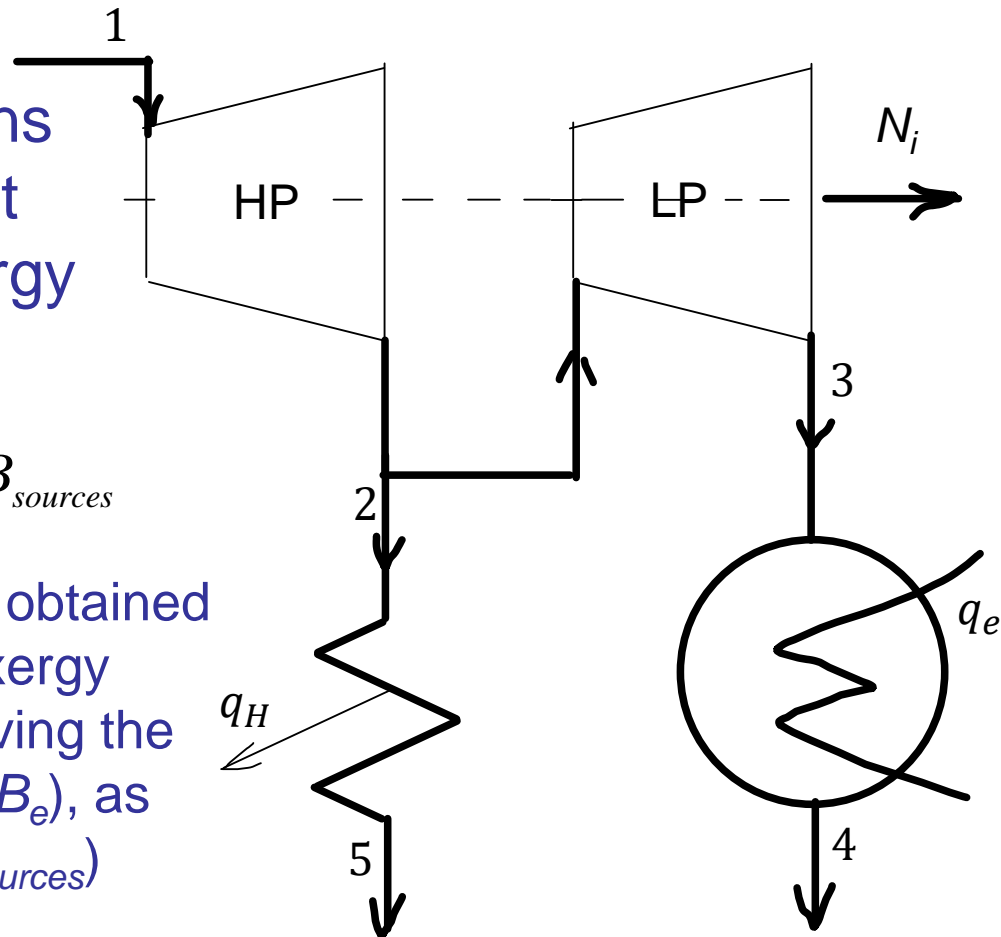


Exergy (11)

- For steady-state conditions the system exergy will not change, and internal exergy losses can be found as

$$\delta B_{int-loss} = B_a - B_e - L - \Delta B_{sources}$$

- thus the exergy losses are obtained as a difference between exergy added (B_a) and exergy leaving the system with working fluid (B_e), as work (L) and as heat ($\Delta B_{sources}$)



Exergy (12)

- Expressed as time-rate loss of exergy, we have

$$\delta \dot{B}_{int-loss} = \dot{B}_a - \dot{B}_e - N - \Delta \dot{B}_{sources}$$

- where

$$\dot{B}_a = W_a [i_a - i_0 - T_0 (s_a - s_0)]$$

$$\dot{B}_e = W_e [i_e - i_0 - T_0 (s_e - s_0)]$$

$$\Delta \dot{B}_{sources} = q_{sources} \frac{T_{sources} - T_0}{T_{sources}}$$

