MENG541 Advanced Thermodynamics

CHAPTER 2 – THE SECOND LAW OF THERMODYNAMICS

Instructor:

Prof. Dr. Uğur Atikol

Chapter 2
The Second Law of Thrmodynamics

Outline

- Closed Systems
  - History
  - One-thermal reservoir
  - Reversibility and irreversible process
  - Two-thermal reservoirs
  - Any number of reservoirs
  - Closed system entropy genaration
- Open Systems

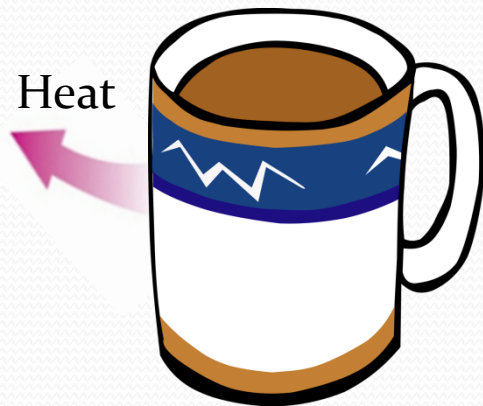# 2nd Law for closed systems

- **History**
  - The early development of the steam engine took place before 1800.
  - The conversion efficiency of these devices at those times were less than 5%.
  - Sadi Carnot (A French Engineer) developed his first theoretical analysis on heat engines in 1824.
  - This was a first step in the development of the 2nd law.
  - The most frequently cited statements of the 2nd law came from Clausius and from Kelvin and Planck.
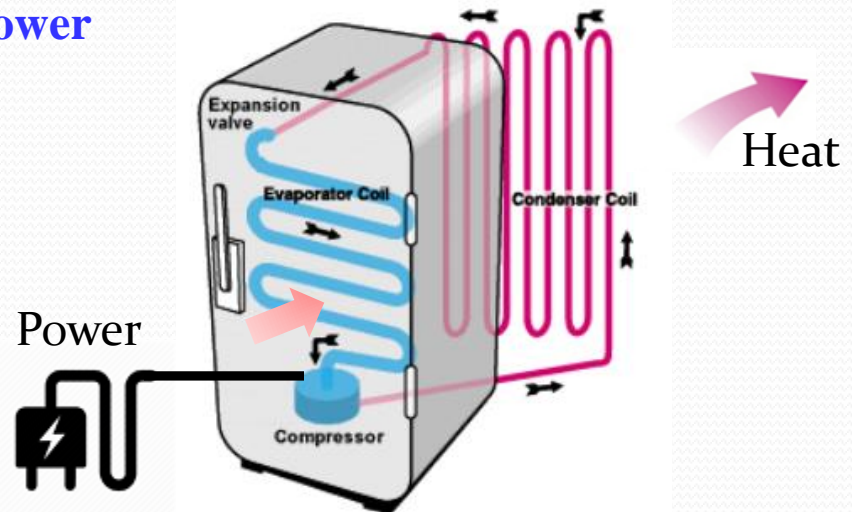
2nd Law for closed systems

- **History**
  - It is observed that heat always flows by itself (spontaneously) from a higher temperature to a region of lower temperature. According to **Clausius** the reverse is impossible without assistance (such as inputing work).

**Heat flows from a cup of hot coffee to cooler room.**

Heat can flow from a refrigerated cold space to warmer room with the aid of electric power

Heat

Heat

Power

2nd Law for closed systems

- **History**
  - The **Kelvin-Plank** concentrate on heat engines.
  - The first law does not bring limitations to conversion of heat to work or work to heat.
 - Example of work conversion into heat would be frictional process.
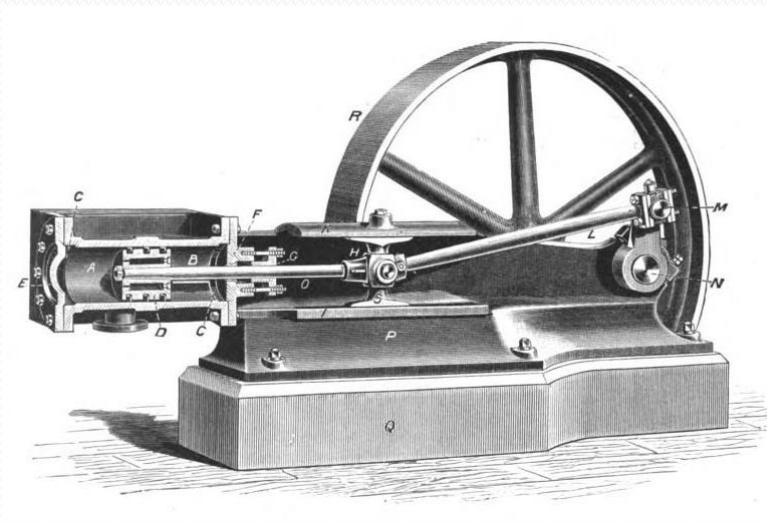
The first law does not bring any restriction on the conversion of heat into work or work into heat.

2nd Law for closed systems

- **Cycle in contact with one temperature reservoir**

  - Plank wrote in 1897: «It is impossible to construct an engine which will work in a complete cycle, and produce no effect except the raising of a weight and cooling of a heat-reservoir.»
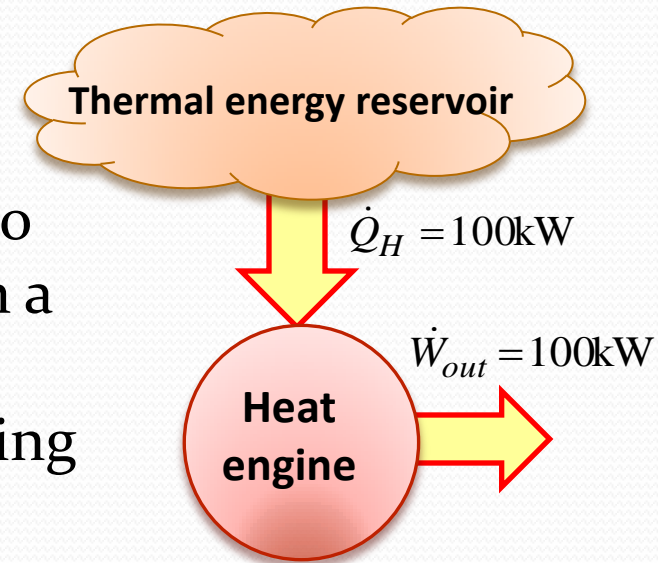
  - A similar statement made in 1851 by William Thomson (Lord Kelvin): «It is impossible, by means of inanimate material agency, to derive mechanical effect from a portion of matter by cooling it below the temperature of the coldest of surrounding objects.

Thermal energy reservoir

$\dot{Q}_H = 100\text{kW}$

$\dot{W}_{out} = 100\text{kW}$

Heat engine

2nd Law for closed systems

- **Cycle in contact with one temperature reservoir**

  - A device which violates the above statements are known as perpetual motion machines of the second kind (PMM2).

  - PMM2 produces work solely by cooling a body.

  - If this was possible a self-acting machine would have produced work by cooling the sea or the earth with no other changes with the interacting system.

Thermal energy reservoir

$\dot{Q}_H = 100\text{kW}$

$\dot{W}_{out} = 100\text{kW}$
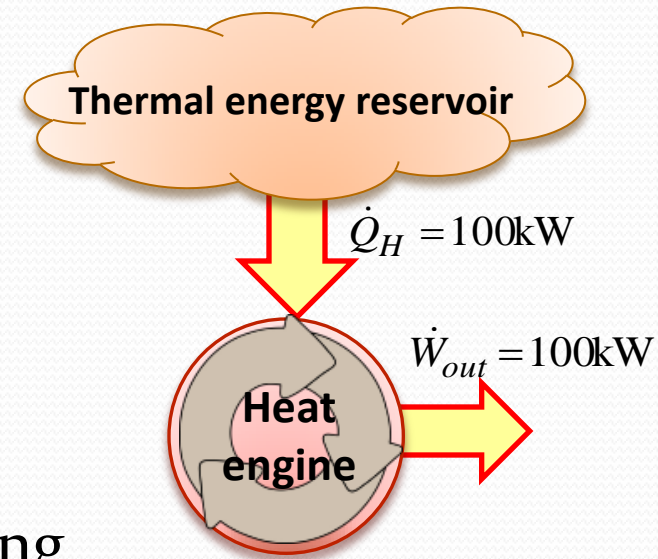
Heat engine

2nd Law for closed systems

- **Cycle in contact with one temperature reservoir**
  - Kelvin-Planck statement implies that the net work produced in a heat engine cycle can not be positive with only one reservoir:

Single Thermal energy reservoir

$\dot{Q}_{cycle,net}$

$\dot{W}_{cycle,net}$
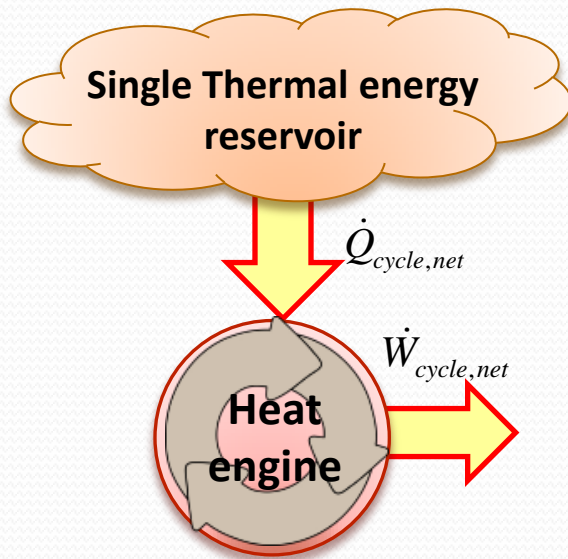
Heat engine

If single reservoir, then first law implies:

$$W_{cycle,net} = Q_{cycle,net} \text{ (or } \oint \delta Q = \oint \delta W)$$

According to Kelvin−Planck, a system undergoing a cycle with a single reservoir cannot deliver a net amount of work to its surroundings. This impossibility reduces to:

$$\oint \delta W \leq 0$$

or in view of the first law for a cycle in a closed system:

$$\oint \delta Q \leq 0$$

2nd Law for closed systems

- **Cycle in contact with one temperature reservoir**
  - For interpreting Kelvin-Planck statement, consider the following example:
  - Net work = Net heat transfer
  - According to Kelvin-Planck net work of cycle can not be positive
  - There may be W_{net} to system
  - Or W_{net} may be zero
  - Analytically this means $\oint \delta W \leq 0$
  - The less than sign implies irreversibilities
  - The equal sign for reversible case
  - Irreversibilities within the system
  - Or *internal irreversibilities* is of interest
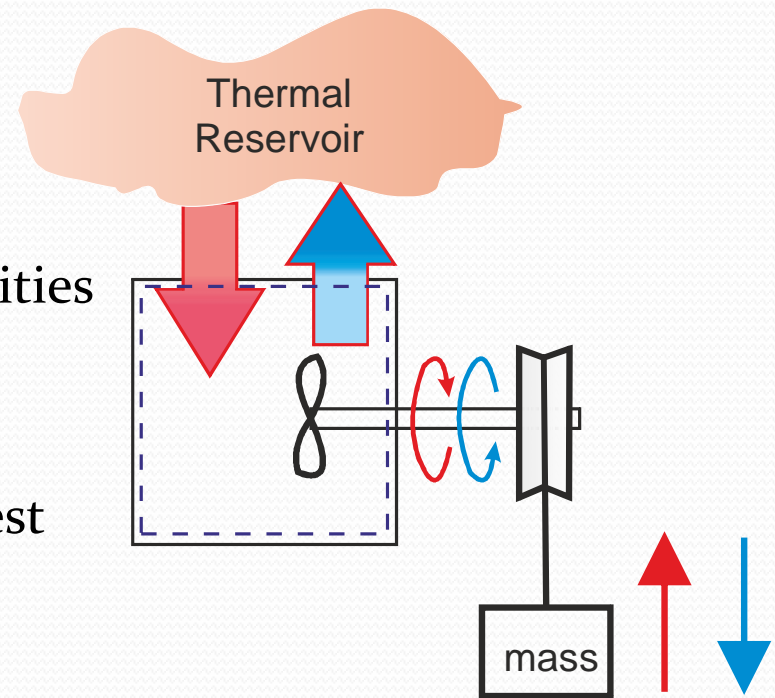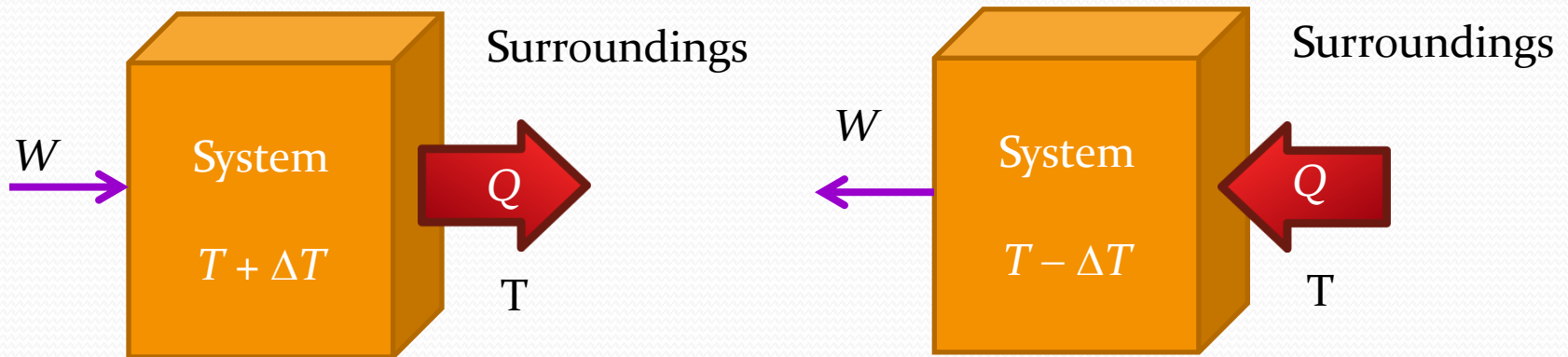
2nd Law for closed systems

- **Reversibility**
  - Two of the main objectives of the 2nd law analysis:
  1. Determining the theorethical best performance of devices
  2. Quantifying the factors that diminish the performance of devices

  It is required to understand the concept of reversibility and reversible process in general.

2nd Law for closed systems

- **Reversible process**
- All heat and work interactions which occur in the initial process can be reversed; they are equal in magnitude but opposite in direction.
- No net history is left in the surroundings when the system gains its initial state.

Surroundings

W → System

Q →

$T + \Delta T$

T

Surroundings

W ← System

← Q

$T - \Delta T$

T

2nd Law for closed systems

- **Irreversible process**
- The reversible process is an idealization. In real life processes are irreversible.
- In real life we have friction, electric resistance, inelasticity (in springs), heat losses (from insulated pipes) etc., which are known as irreversibilities.
- Irreversibilities can be reduced but we can not completely eliminate them.
- Any system which is returned to its initial state after going through an irreversible process will leave a history in the surroundings due to irreversibilities.
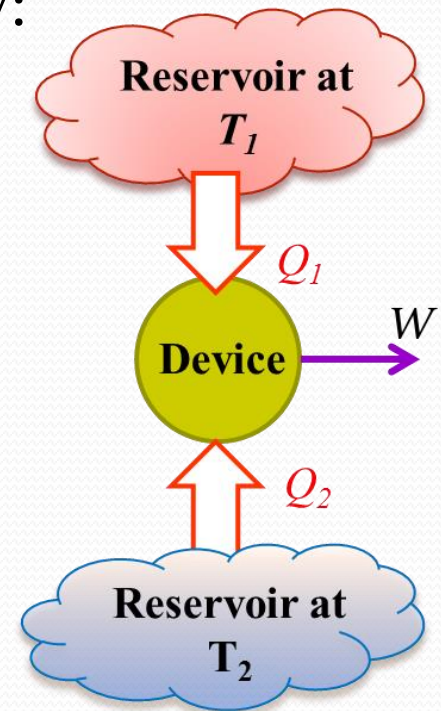
2nd Law for closed systems

- **Cycles with Two Thermal Reservoirs**
  - Sadi Carnot introduced the reversible cycle in 1824.
  - Carnot's principle:
    1. $\eta_{th,irrev}$ is always less than $\eta_{th,rev}$ operating between the same reservoirs.
    2. Thermal efficiencies of all reversible heat engines operating between the same reservoirs are equal.
  - An independent absolute temperature scale may be defined which is independent of the nature of the measuring substance (such as water).

2nd Law for closed systems

- **Cycles with Two Thermal Reservoirs**
  - Mathematically the dependence of (Q_2/Q_1) on T_1 and T_2 can be expressed by:

$$\left(\frac{-Q_2}{Q_1}\right)_{rev} = f(T_2, T_1)$$

  - Note that f is an unknown function
  - T_1 and T_2 are readings from the scale of one thermometer
  - Consider the following:

Reservoir at T_1

Q_1

Device

W

Q_2

Reservoir at T_2
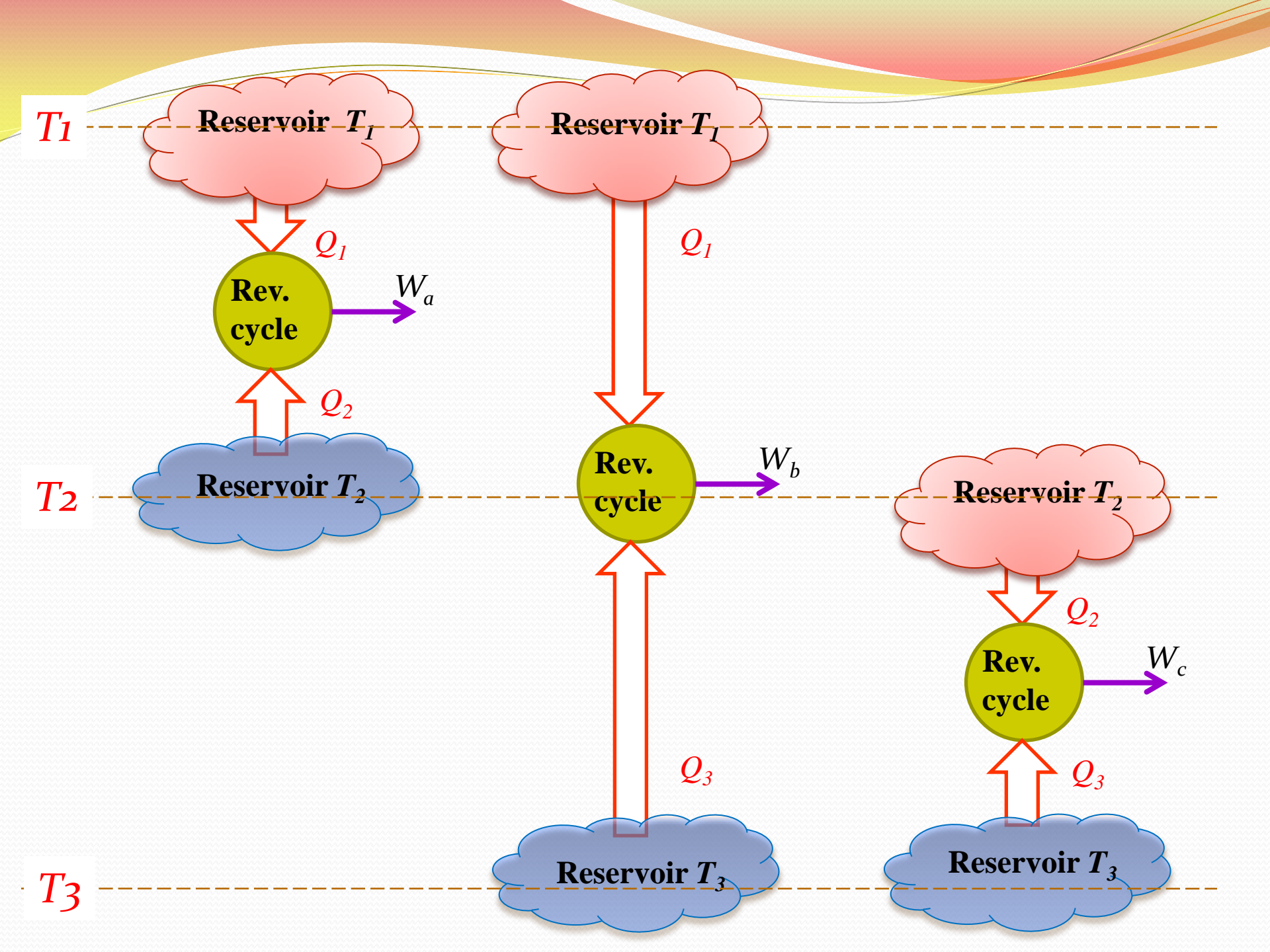
2nd Law for closed systems

In that case we can write the following equations:

$$\left(\frac{-Q_3}{Q_1}\right)_{rev} = f(T_3, T_1)$$

$$\left(\frac{-Q_3}{-Q_2}\right)_{rev} = f(T_3, T_2)$$

$$\underbrace{\left(\frac{-Q_2}{Q_1}\right)_{rev}}_{f(T_2, T_1)} = \frac{f(T_3, T_1)}{f(T_3, T_2)}$$

Dividing these two equations we obtain:

$$f(T_2, T_1) = \frac{f(T_3, T_1)}{f(T_3, T_2)}$$

2nd Law for closed systems

$$f(T_2, T_1) = \frac{f(T_3, T_1)}{f(T_3, T_2)}$$

$\uparrow$

Does not depend on T_3, therefore we can re-write as:

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

or letting $f'' = 1/f'$:

$$\left(\frac{-Q_2}{Q_1}\right)_{rev} = f(T_2, T_1) = \frac{f''(T_2)}{f''(T_1)}$$

At this point the choice of the mathematical form of $f''(T)$ is completely arbitrary. Here Kelvin scale is defined by selecting $f''(T)=T$. Therefore, for a Carnot heat engine operating between T_1 and T_2:

$$\left|\frac{Q_2}{Q_1}\right| = \frac{T_2}{T_1}$$
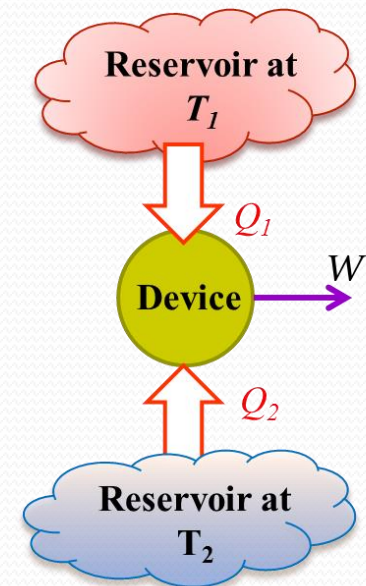
2nd Law for closed systems

As a result, by introducing the concept of the thermodynamic temperature scale (Kelvin temperature scale) for a reversible heat engine we can write:

$$\left| \frac{Q_2}{Q_1} \right| = \frac{T_2}{T_1} \quad \text{or} \quad \left(\frac{-Q_2}{Q_1} \right) = \frac{T_2}{T_1}$$

The following second law statement can be derived:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \leq 0$$

This statement is a generalization of the Kelvin-Planck statement and it is independent of the sign of W.

Reservoir at T_1

Q_1

Device $\longrightarrow W$

Q_2

Reservoir at T_2

2nd Law for closed systems

- **Cycles in contact with any Number of Thermal Reservoirs**

The Kelvin-Planck statement which was stated as $\oint \delta Q \leq 0$ for a single reservoir can be written as:

$$\frac{Q_1}{T_1} \leq 0$$

where T_1 is the temperature of the single reservoir. For two and n number of reservoirs:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \leq 0$$

and

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \cdots + \frac{Q_n}{T_n} \leq 0$$

2nd Law for closed systems

- **Cycles in contact with any Number of Thermal Reservoirs**

Consider a continuous variation of system boundary temperature as the cycle is performed in contact with an infinite order of reservoirs, each supplying a heat interaction of δQ. The above equation can be expressed as:

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

T is in Kelvin (or in Rankine) at the system boundary that is crossed by δQ. For reversible cycles equal sign is used, such that, when the cycles are reversed, the energy interactions are reversed but their magnitudes are unchanged.

2nd Law for closed systems

- **Cycles in contact with any Number of Thermal Reservoirs**

The concept of entropy evolves from the above equation, such that:

$$\oint \frac{\delta Q_{rev}}{T} = 0$$

In the above expression, $\delta Q_{rev}/T$ represents a property since the net change during a reversible cycle is zero. This property is called entropy:

$$dS = \frac{\delta Q_{rev}}{T}$$

$\rightarrow$The term «entropy» was coined by Clausius in 1865.

$\rightarrow$However, the same property was discovered before by Rankine. He called it «thermodynamic function» and represented it with ϕ instead of S and regarded above equation as the *general equation of thermodynamics*.

2nd Law for closed systems

- **Process in contact with any Number of Thermal Reservoirs**

Consider any arbitrary process (whose path and energy is not specified) taking place between states 1 and 2 :

$$S_2 - S_1 = \frac{\delta Q_{rev}}{T}$$

Process 1–2
(reversible or irreversible)

2

1

Process 2–1
(internally reversible)
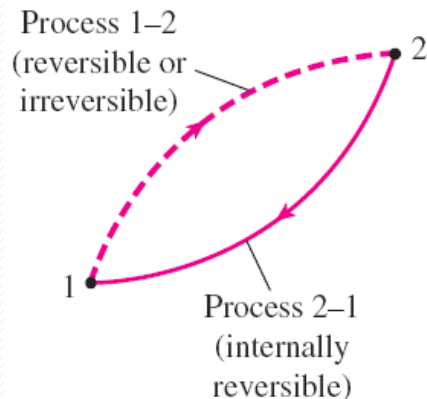
A cycle composed of a reversible and an irreversible process.

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

$$\Rightarrow \int_1^2 \frac{\delta Q}{T} + \int_2^1 \frac{\delta Q_{rev}}{T} \leq 0$$

$$\Rightarrow \underbrace{\int_1^2 \frac{\delta Q}{T}}_{\substack{\text{Entropy} \\ \text{transfer} \\ \text{(Nonproperty)}}} \leq \underbrace{S_2 - S_1}_{\substack{\text{Entropy} \\ \text{change} \\ \text{(Property)}}}$$

2nd Law for closed systems
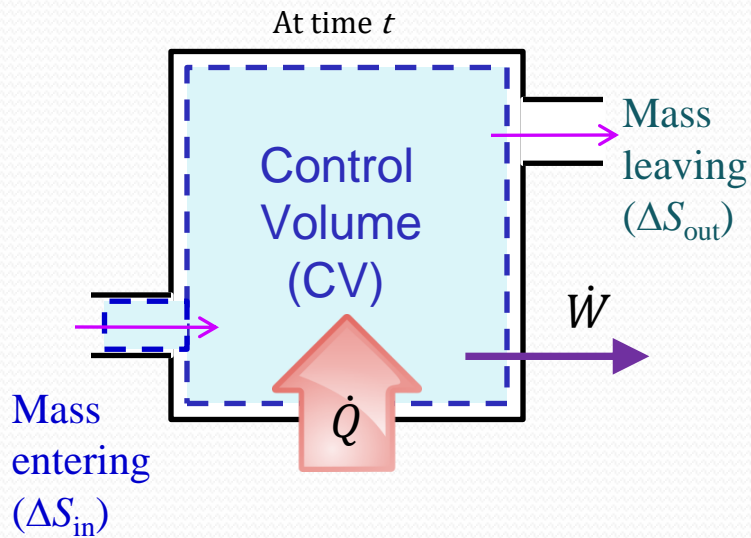
- **Closed-system entropy generation**

For a process the second law requires that the entropy transfer never exceeds the entropy change.

$$\Rightarrow \underbrace{\int_1^2 \frac{\delta Q}{T}}_{\substack{\text{Entropy} \\ \text{transfer} \\ \text{(Nonproperty)}}} \leq \underbrace{S_2 - S_1}_{\substack{\text{Entropy} \\ \text{change} \\ \text{(Property)}}}$$

This inequality can be transformed into an equality by the introduction of the concept of **entropy generation** (or **entropy production**).

$$\Rightarrow S_{gen} = S_2 - S_1 - \int_1^2 \frac{\delta Q}{T} \geq 0$$

2nd Law for open systems

At time t

Control Volume (CV)

Mass leaving (ΔS_{out})

$\dot{W}$

$\dot{Q}$

Mass entering (ΔS_{in})

At time $t+\Delta t$

Control Volume (CV)

Mass leaving (ΔS_{out})

$\dot{W}$

$\dot{Q}$

Mass entering (ΔS_{in})

The light blue area can be assumed to be fixed in mass. Therefore it is said to be control mass or closed system.

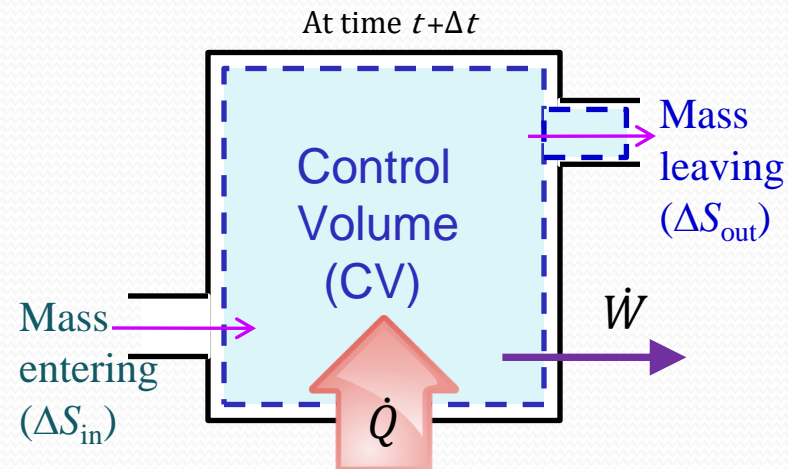At time t : $S_{closed,t} = S_{open,t} + \Delta S_{in}$

At time $t+\Delta t$: $S_{closed,t+\Delta t} = S_{open,t+\Delta t} + \Delta S_{out}$

$$\Delta S_{in,out} = (s\Delta m)_{in,out} = (s\dot{m})_{in,out}\Delta t$$

If entropy generation from t to $t+\Delta t$ is ΔS_{gen} :

$$\Delta S_{gen} = S_{open,t+\Delta t} - S_{open,t} - \frac{\dot{Q}_i}{T_i}\Delta t + (\dot{m}s)_{out}\Delta t$$
$$-(\dot{m}s)_{in}\Delta t \geq 0$$

obtained from $S_{gen} = S_2 - S_1 - \int_1^2 \frac{\delta Q}{T} \geq 0$ and considering any number of heat transfer sources i.

2nd Law for open systems

Consider the last equation obtained:

$$\Delta S_{gen} = S_{open,t+\Delta t} - S_{open,t} - \frac{\dot{Q}_i}{T_i}\Delta t + (\dot{m}s)_{out}\Delta t - (\dot{m}s)_{in}\Delta t \geq 0$$

Dividing by Δt or differentiating w.r.t. t:

$$\underbrace{\dot{S}_{gen}}_{\substack{\text{Entropy} \\ \text{generation} \\ \text{rate}}} = \underbrace{\frac{dS}{dt}}_{\substack{\text{Rate of entropy} \\ \text{accumulation} \\ \text{inside the} \\ \text{control} \\ \text{volume}}} - \underbrace{\sum_i \frac{\dot{Q}_i}{T_i}}_{\substack{\text{Entropy} \\ \text{transfer} \\ \text{rate due to} \\ \text{heat transfer}}} + \underbrace{\sum_{out} m\dot{s} - \sum_{in} m\dot{s}}_{\substack{\text{Net entropy flow} \\ \text{rate out of the} \\ \text{control volume} \\ \text{due to mass flow}}} \geq 0$$

Note: Work transfer is not accompanied by entropy transfer.