Second Law of Thermodynamics

Presentation Outline

- Overview
- Second Law of Thermodynamics
- Heat Engine
- Heat Pump
- Second Law Statements
- Carnot Cycle
- Concept of Entropy

Overview

- According to the First Law of Thermodynamics a 100% efficient cycle (in principle) can be in existence.

- However, Second Law of Thermodynamics states clearly that it is not possible.

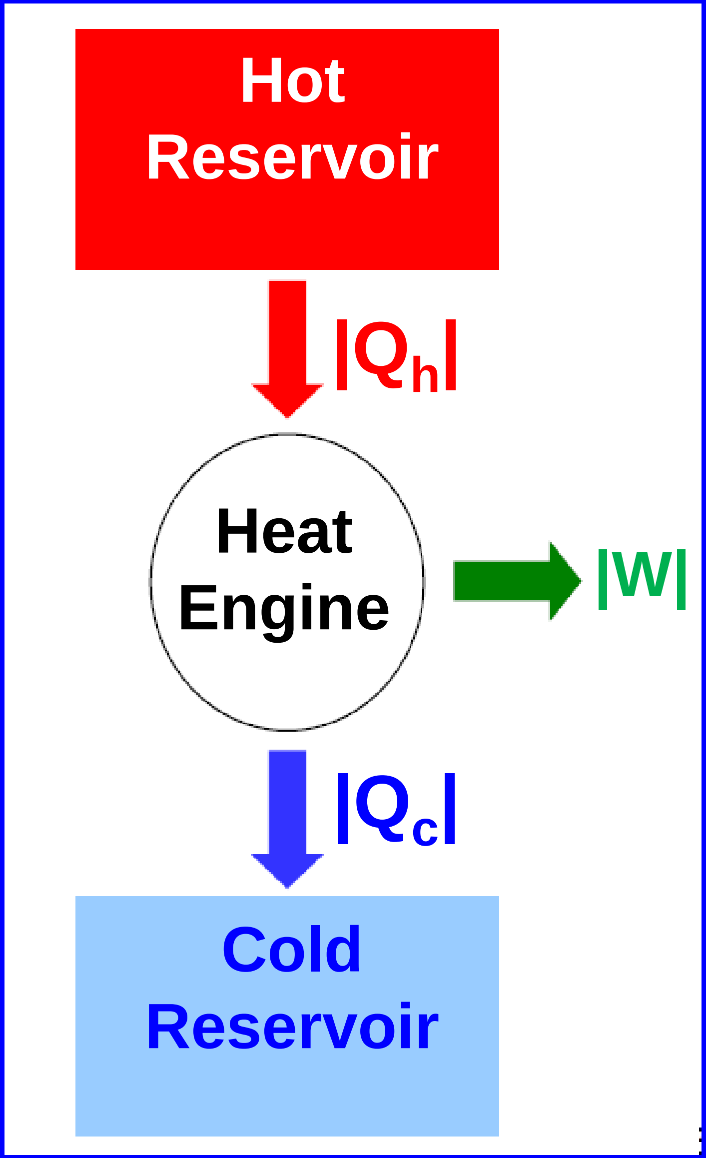
- Second Law is an expression of the fact that some heat must always be rejected during the cycle and hence the cycle efficiency is always less than 100%.

Second Law of Thermodynamics

- Second Law of Thermodynamics may be stated in the following form:

  It is impossible to construct a system which will operate in a cycle, extract heat from a reservoir and do an equivalent amount of work on the surroundings.

Heat Engine



Heat Engine contd..

- A Heat Engine operates in a cycle, converting heat into work and then return to original state at the end of the cycle.

- In each cycle, heat engine takes in heat $|Q_h|$ from a “Hot Reservoir”, converts some of it into work $|W|$, and discharges the remaining heat $|Q_c|$ into a “Cold Reservoir”

Efficiency of a Heat Engine

Efficiency (η) = $\dfrac{\text{Work done per cycle}}{\text{Heat input per cycle}}$

$$\eta = \frac{|W|}{|Q_h|}$$

- Since the Heat Engine returns to original state at the end of each cycle, $\Delta U(cycle) = 0$
- Hence by applying First Law $Q - W = 0$
- Hence $|W| = |Q_h| - |Q_c|$

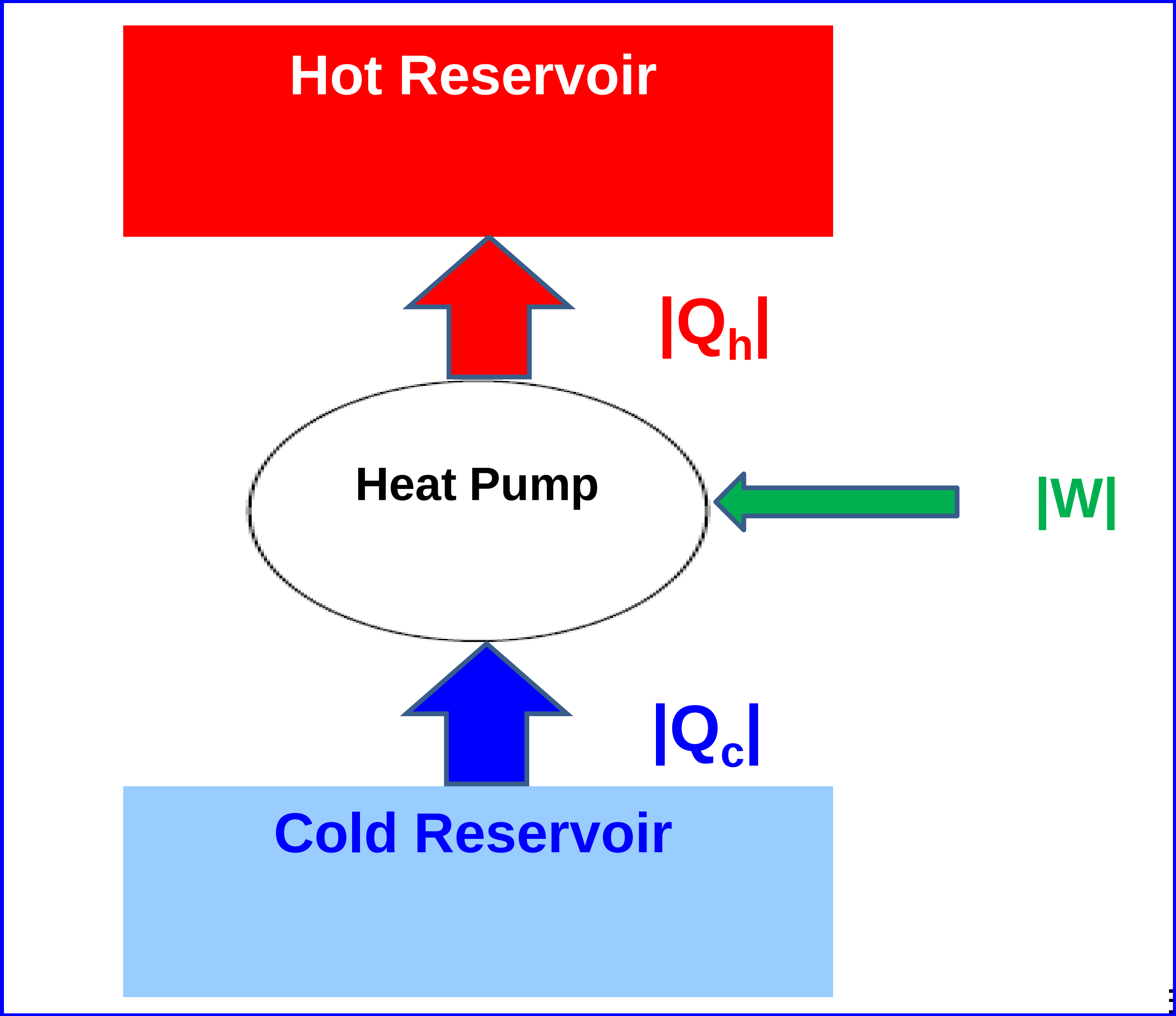
Efficiency of a Heat Engine contd..

$$\eta = \frac{|Q_h| - |Q_c|}{|Q_h|}$$

- Hence

$$\eta = 1 - \frac{|Q_c|}{|Q_h|}$$

Heat Pump



Heat Pump contd..

- Heat Pumps and Refrigerators are Heat Engines running in the reverse direction.
- Refrigerator removes heat from a cold reservoir and transfers it into surroundings, keeping food in the reservoir cold.
- Heat Pump takes energy from cold reservoir and discharges it into a building or occupancy space, thereby warming it.
- In either case, energy must be supplied to the machine.

Heat Pump contd..

- To measure the performance of a Refrigerator or Heat Pump the *Coefficient of Performance* (CoP) is used.
- In the case of a Refrigerator one wants to know the quantity of heat absorbed from the cold reservoir and hence Q_c is the important factor in deciding the CoP value.
- In the case of a Heat Pump the quantity of heat transferred to the hot reservoir (Q_h) is the important factor in deciding the CoP value.

CoP of a Refrigerator

- The Coefficient of Performance of a Refrigerator is expressed as

$$(CoP)_R = \frac{|Q_c|}{|W|}$$

$$(CoP)_R = \frac{|Q_c|}{|Q_h| - |Q_c|}$$

CoP of a Heat Pump

- The Coefficient of Performance of a Heat Pump is expressed as

$$(CoP)_{HP} = \frac{|Q_h|}{|W|}$$

$$(CoP)_{HP} = \frac{|Q_h|}{|Q_h| - |Q_c|}$$

Coefficient of Performance

- It can be shown that

$$(CoP)_{HP} = (CoP)_R + 1$$

- For most practical refrigeration cycles the Coefficient of Performance is in the range of 4 – 5.

Second Law Statements

- There are two classical statements to describe the Second Law of Thermodynamics. They are
  - Kelvin Plank Statement
  - Clausius Statement

- Let us consider the above statements separately.

The Kelvin-Plank Statement

- “It is impossible to construct a system which will operate in a cycle, extract heat from a hot reservoir, and only to do an equivalent amount of work on the surroundings”.
- This implies that there cannot exist any machine that transforms all the heat it absorbs into work.
- Hence, no machine can show 100% efficiency.

The Clausius Statement

- “It is impossible to construct a system which will operate in a cycle and transfer heat from a cooler to a hotter body without work being done on the system by the surroundings.”
- This implies that if a machine is constructed to absorb heat from a cooler body, that machine will consume energy from the surroundings.

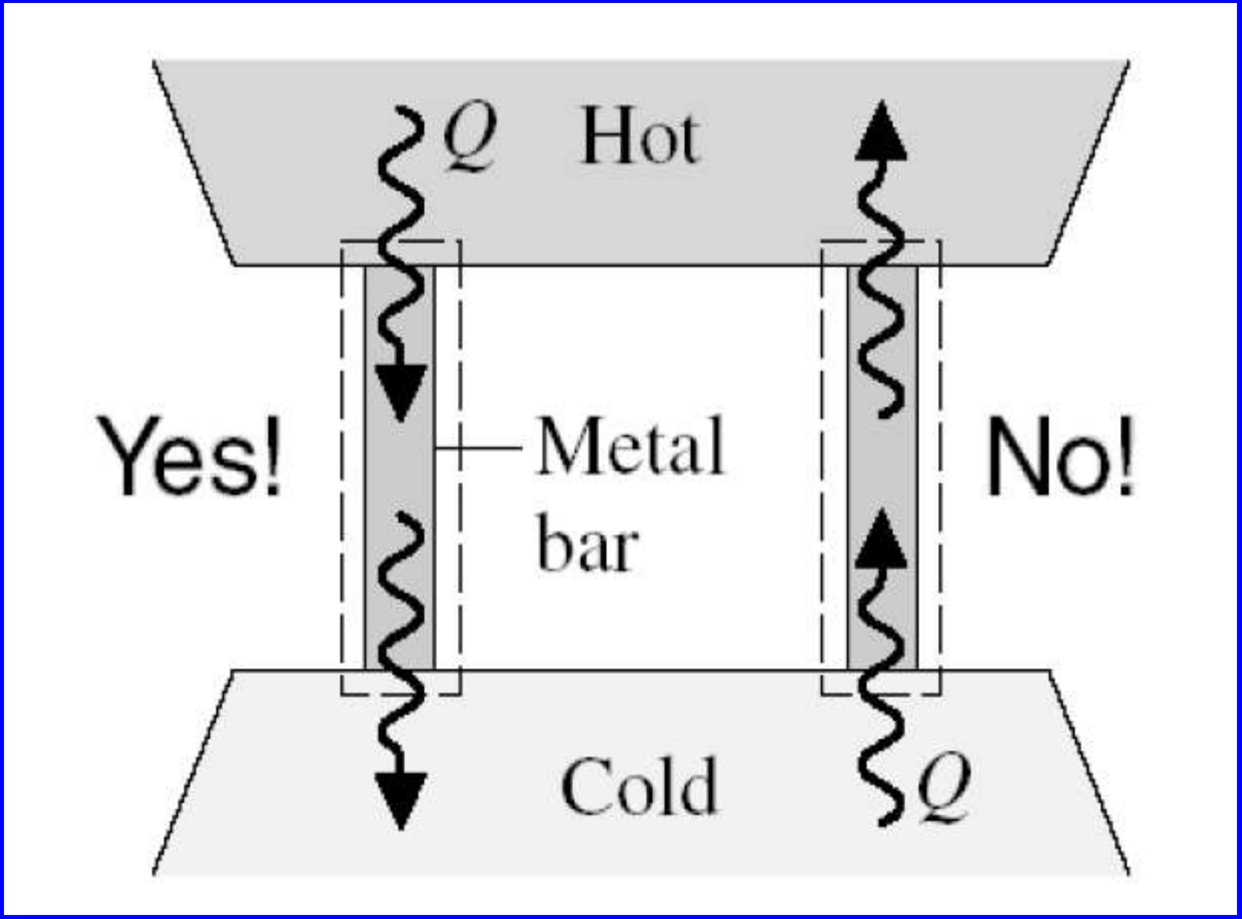
Second Law Statements

- The Kelvin-Plank statement introduces the concept of Heat Engine.

- The Clausius statement introduces the concept of Heat Pump (or Refrigerator).

- It can be shown that the Kelvin-Plank and the Clausius statements are equivalent.

Second Law Statements



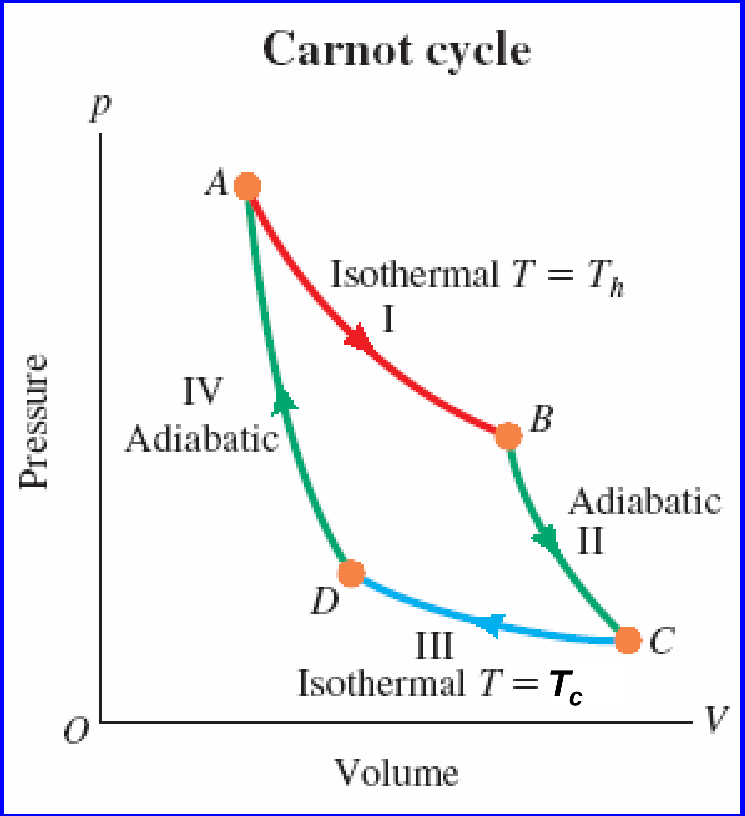
Carnot Cycle

- It can be shown from the Second Law of Thermodynamics that no Heat Engine can be more efficient than the reversible Heat Engine described by *Sadi Carnot*.

- This is known as the Carnot Cycle (Carnot Heat Engine)

Carnot Cycle contd..

- The work done during the Carnot cycle is the area enclosed by the curve in the p-V diagram.

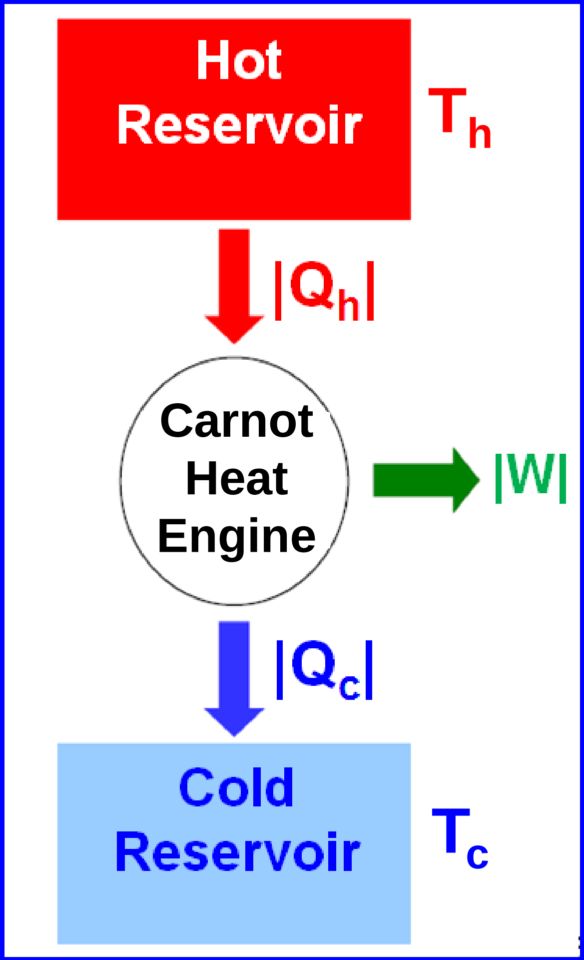


Carnot Cycle Efficiency

- Through analysis, Efficiency of the Carnot Heat Engine cycle can be related to the reservoir temperatures as expressed below:

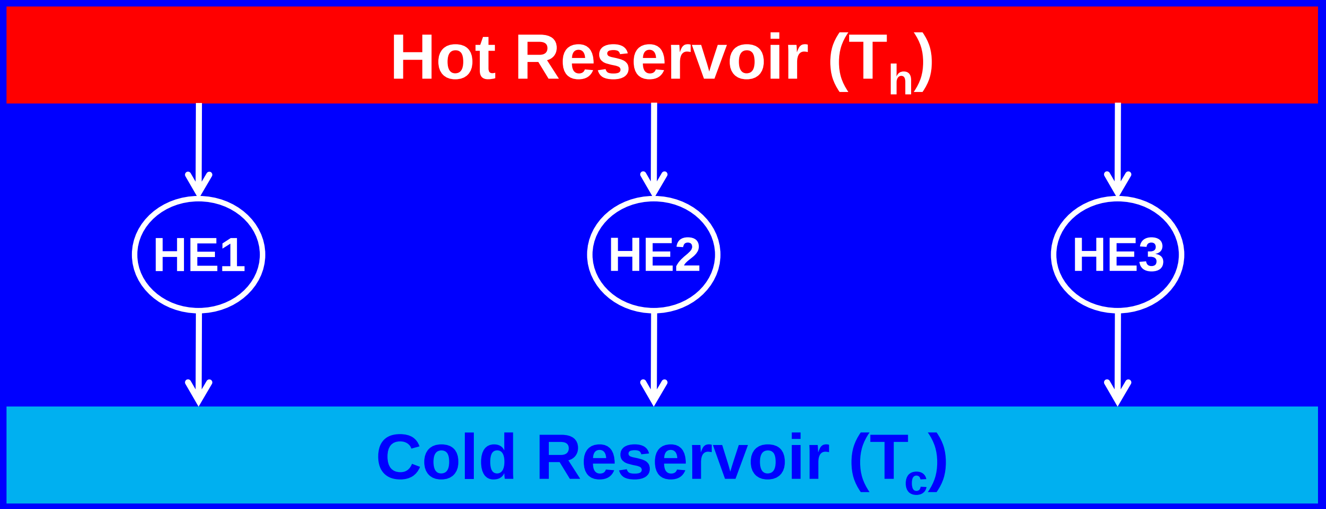
$$\eta_C = 1 - \frac{T_c}{T_h}$$

- The Carnot Heat Engine is the most efficient Heat Engine possible that operates between any two given temperatures.



Carnot Cycle Efficiency contd..

- All reversible Heat Engines operating between the same two reservoirs have the same Carnot efficiency.



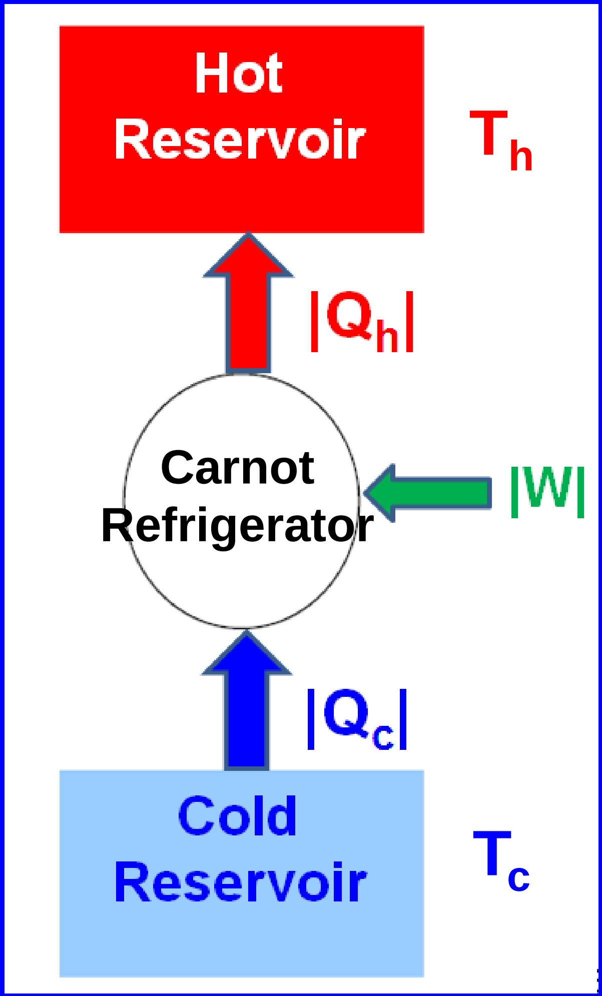
- Hence $\eta_{C1} = \eta_{C2} = \eta_{C3} = \ldots\ldots\ldots\ldots\ldots = \eta_{Cn}$

CoP of a Carnot Refrigerator

- Through analysis, CoP of a Carnot Refrigerator cycle can be related to the reservoir temperatures as expressed below:

$$(CoP)_R = \frac{T_c}{T_h - T_c}$$

- The Carnot Refrigerator has the highest CoP value possible that operates between any two given temperatures.

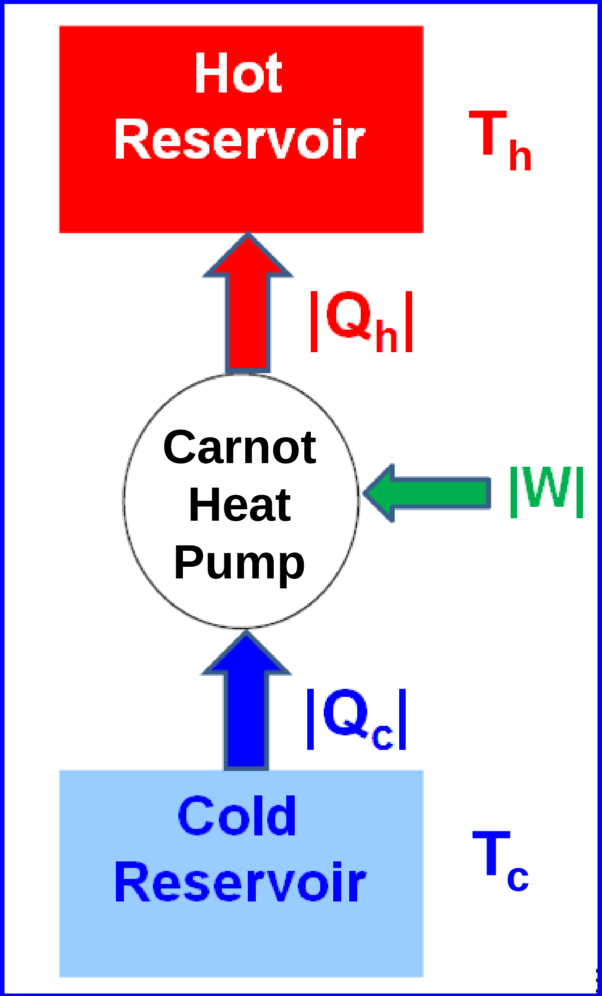


CoP of a Carnot Heat Pump

- Through analysis, CoP of a Carnot Heat Pump cycle can be related to the reservoir temperatures as expressed below:

$$(CoP)_{HP} = \frac{T_h}{T_h - T_c}$$

- The Carnot Heat Pump has the highest CoP value possible that operates between any two given temperatures.



Concept of Entropy

- The property *Entropy* arises as a consequence of the Second Law of Thermodynamics, in much the same way as the property internal energy arises from the First Law.
- Entropy is a measure of how evenly energy is distributed in a system.
- In a physical system, entropy provides a measure of the amount of energy that <u>cannot</u> be used to do work.

Concept of Entropy contd..

- As with internal energy, only the changes in entropy are generally of interest.
- Entropy is a thermodynamic property, however, it can be expressed as a function of other thermodynamic properties which can be measured by experiments involving real processes.
- Entropy per unit mass is known as the specific entropy (s) and its units are (J/kgK).

Definition of Entropy

- Whenever a system undergoes a cycle
  - If the cycle is reversible then,

$$\oint \left(\frac{dQ}{T} \right) = 0$$

  - If the cycle is irreversible then,

$$\oint \left(\frac{dQ}{T} \right) < 0$$

  - In general $\oint \left(\frac{dQ}{T} \right) \leq 0$

Definition of Entropy contd..

Apply First Law for a reversible process

$$dQ - dW = dU$$

$$dQ - pdV = dU$$

$$dQ = dU + pdV$$

For a perfect gas

$$dQ = c_v dT + RT\frac{dV}{V}$$

Definition of Entropy contd..

Hence by dividing through by T

$$\frac{dQ}{T} = \frac{c_v dT}{T} + \frac{RdV}{V}$$

For a reversible adiabatic process

$$dQ = 0$$

Hence

$$\frac{dQ}{T} = \frac{c_v dT}{T} + \frac{RdV}{V} = 0$$

Definition of Entropy contd..

Therefore, for a reversible adiabatic process

$$\frac{dQ}{T} = 0$$

For any other reversible process

$$\frac{dQ}{T} \neq 0$$

Hence for all working substances for any reversible process

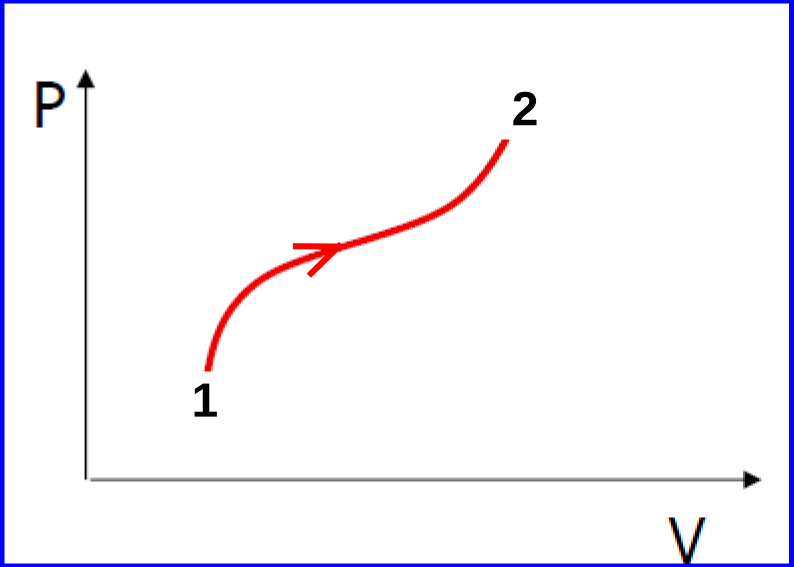
$$ds = \frac{dQ}{T}$$ where s is the entropy

Definition of Entropy contd..

- The change of entropy is more important than its absolute value
- By integration

$$\int_1^2 ds = \int_1^2 \frac{dQ}{T}$$

$$s_2 - s_1 = \int_1^2 \frac{dQ}{T}$$



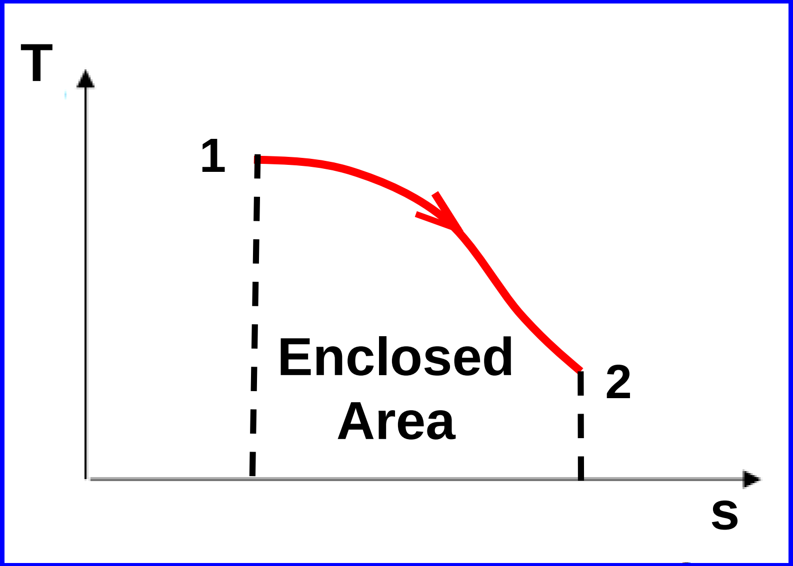
Definition of Entropy contd..

Change of entropy in any reversible process

$$ds = \frac{dQ}{T}$$

$$dQ = Tds$$

$$Q = \int_1^2 Tds$$



Heat transfer in a reversible process = Area enclosed by the T-s diagram.

Definition of Entropy contd..

- Entropy of any closed system which is thermally isolated from the surroundings either increases or, if the process undergone by the system is reversible, remains constant.

$$\boxed{s_2 - s_1 = \int_1^2 \frac{dQ}{T}}$$ for a reversible process

- For thermally isolated system $\boxed{dQ = 0}$

- Hence $\boxed{s_2 - s_1 = 0}$ $\boxed{s_1 = s_2}$

Change of Entropy

- Let us derive expressions for change of entropy related to standard non-flow processes.
- Following assumptions are made during the derivations
  - Working fluid is a perfect gas
  - All processes are reversible
  - Analysis is based on unit mass

Change of Entropy contd..

1. Constant Volume Process

Change of Entropy

$$s_2 - s_1 = \int_1^2 \frac{dQ}{T}$$

$$dQ = c_v dT$$

$$s_2 - s_1 = \int_1^2 \frac{c_v dT}{T} = c_v \ln\left(\frac{T_2}{T_1}\right)$$

Change of Entropy contd..

2. Constant Pressure Process

Change of Entropy

$$s_2 - s_1 = \int_1^2 \frac{dQ}{T}$$

$$dQ = c_p dT$$

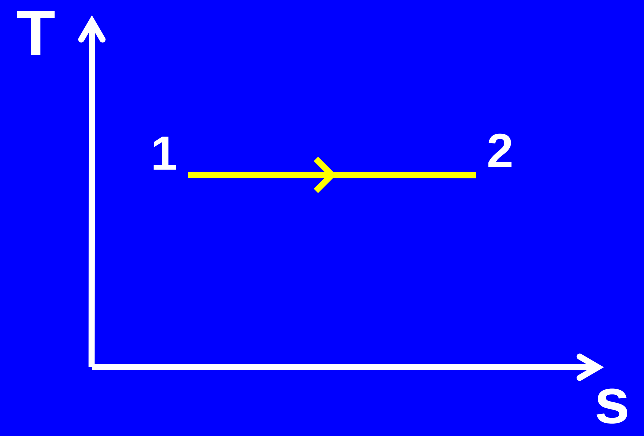
$$s_2 - s_1 = \int_1^2 \frac{c_p dT}{T} = c_p \ln\left(\frac{T_2}{T_1}\right)$$

Change of Entropy contd..

3. Isothermal Process

Heat transfer

$$Q = Tds = T\left(s_2 - s_1\right)$$



From First Law

$$dQ - dW = du \qquad dQ = du + dW \qquad dQ = du + pdV$$

Also $du = c_v dT$

Hence $dQ = c_v dT + pdV$

Change of Entropy contd..

3. Isothermal Process contd..

$$dT = 0$$

Hence $$dQ = pdV$$

Also $$pV = RT$$

Hence $$dQ = RT\frac{dV}{V}$$

Change of Entropy $$s_2 - s_1 = \int_1^2 \frac{dQ}{T}$$

Change of Entropy contd..

3. Isothermal Process contd..

Change of Entropy

$$s_2 - s_1 = \int_1^2 \frac{dQ}{T} = \int_{V_1}^{V_2} R\frac{dV}{V} = R\int_{V_1}^{V_2} \frac{dV}{V} = R\ln\left(\frac{V_2}{V_1}\right)$$

Also $p_1V_1 = p_2V_2$

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

Change of Entropy contd..

3. Isothermal Process contd..

Heat transfer

$$Q = T\left(s_2 - s_1\right) = RT\ln\left(\frac{V_2}{V_1}\right) = RT\ln\left(\frac{p_1}{p_2}\right)$$

Change of Entropy contd..

4. Polytropic Process

From First Law

$$dQ - dW = du \qquad dQ = du + dW$$

$$dQ = du + pdV$$

Also $du = c_v dT$ $\qquad pV = RT$

$$dQ = c_v dT + RT\,\frac{dV}{V}$$

Change of Entropy contd..

4. Polytropic Process contd..

$$ds = \frac{dQ}{T} = c_v \frac{dT}{T} + R\frac{dV}{V}$$

Change of Entropy

$$s_2 - s_1 = c_v \int_{T_1}^{T_2} \frac{dT}{T} + R\int_{V_1}^{V_2} \frac{dV}{V} = c_v \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{V_2}{V_1}\right)$$