

Rohini College Of Engineering And Technology

Department Of Mechanical Engineering



ME3391 ENGINEERING THERMODYNAMICS

UNIT II

SECOND LAW OF THERMODYNAMICS

MODULE-2

SECOND LAW OF THERMODYNAMICS

State the limitations of first law of thermodynamics?

1. First Law places no restriction on the direction of a process.
2. It does not ensure whether the process is feasible or not.
3. This law does not differentiate heat and work. It is concerned with the quantity of energy and the transformation of energy from one form to another with no regard to its quality.

Aspects of the second law

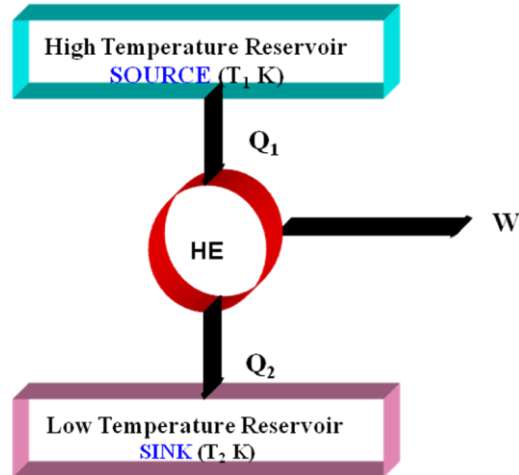
1. To identify the direction of process.
2. Establishing conditions for equilibrium.
3. It also asserts that energy has quality as well as quantity.
3. It is also used in determining the theoretical limits for the performance of heat engines and refrigerators.
4. Defining a temperature scale independent of the properties of any thermometric substance.

Thermal Energy Reservoir (TER): It is a hypothetical body with a relatively large thermal energy capacity that can supply or absorb finite amount of heat without undergoing any change in temperature. Examples: Oceans, rivers, atmospheric air etc.

- TER that supplies energy in the form of heat is called a **source**
- TER that absorbs energy in the form of heat is called a **sink**

Heat Engines: Heat engine is a cyclic device, used to convert heat to work. Heat engine can be characterized by the following points.

1. They receive heat from a high temperature source (solar energy, oil-furnace etc.)
2. They convert part of this heat to work (usually in the form of a rotating shaft)
3. They reject the remaining waste heat to a low temperature sink (the atmosphere, rivers, etc)
4. They operate on a cycle.



Q_1 = amount of heat supplied to steam in boiler from a high-temperature source.

Q_2 = amount of heat rejected from steam in condenser to a low temperature sink.

W = net work output of this heat engine.

Thermal efficiency: The fraction of the heat input that is converted to net work output is a measure of the performance of the heat engine.

$$\text{Thermal efficiency}(\eta) = \frac{\text{Net work output}}{\text{Total heat input}}$$

$$\eta_{\text{th}} = \frac{W}{Q_1}$$

$$\eta_{\text{th}} = 1 - \frac{Q_2}{Q_1}$$

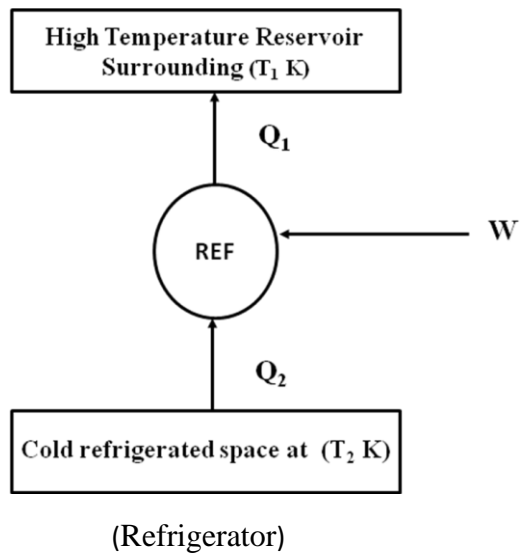
Refrigerator: Refrigerators are cyclic devices, used to transfer heat from a low temperature medium to a high temperature medium.

The working fluid used in the refrigeration cycle is called a refrigerant. The most frequently used refrigeration cycle is the vapor-compression refrigeration cycle.

Coefficient of Performance (COP)

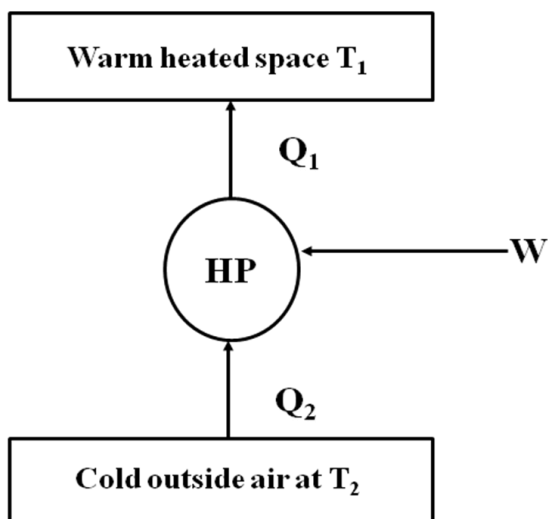
$$\text{COP}_R = \frac{\text{Desired output}}{\text{Required input}} = \frac{Q_2}{W}$$

$$\text{COP}_R = \frac{Q_2}{Q_1 - Q_2}$$



Heat Pumps: Heat pumps are another cyclic devices, used to transfer heat from a low temperature medium to a high temperature medium.

The objective of a heat pump is to maintain a heated space at a high temperature. This is accomplished by absorbing heat from a low temperature source, such as cold outside air in winter and supplying this heat to the high temperature medium such as a house.



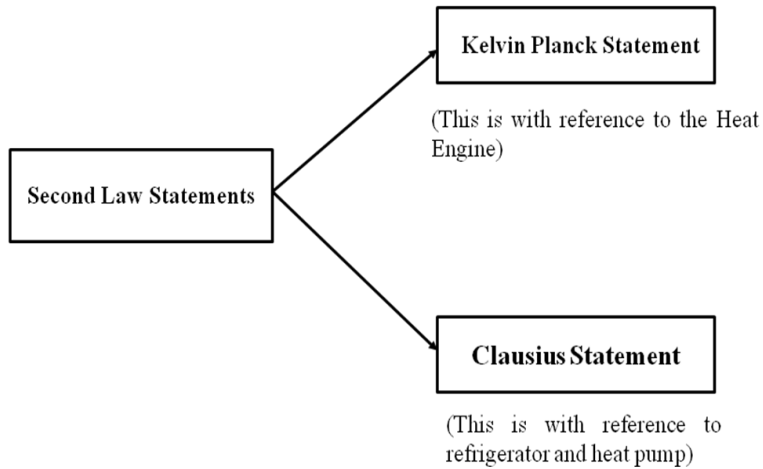
$$\text{COP}_{\text{HP}} = \frac{\text{Desired output}}{\text{Required input}} = \frac{Q_1}{W}$$

$$\text{COP}_{\text{HP}} = \frac{Q_1}{Q_1 - Q_2}$$

Relation between COP_{HP} and COP_{R}

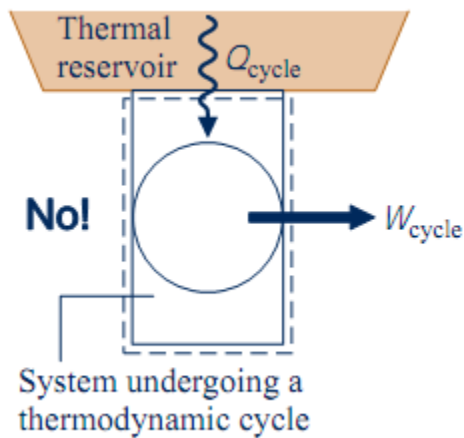
$$\text{COP}_{\text{HP}} = \text{COP}_{\text{R}} + 1$$

Statements of Second Law



Kelvin-Planck Statement of the Second law

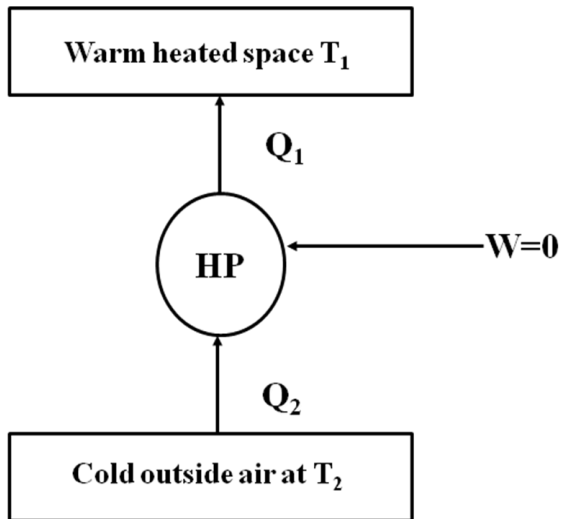
It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work.



(A heat engine that violates the Kelvin-Planck statement)

Clausius Statement:

It is impossible to construct a device that operates in a cycle and produce no effect other than the transfer of heat from a low temperature body to a high temperature body.

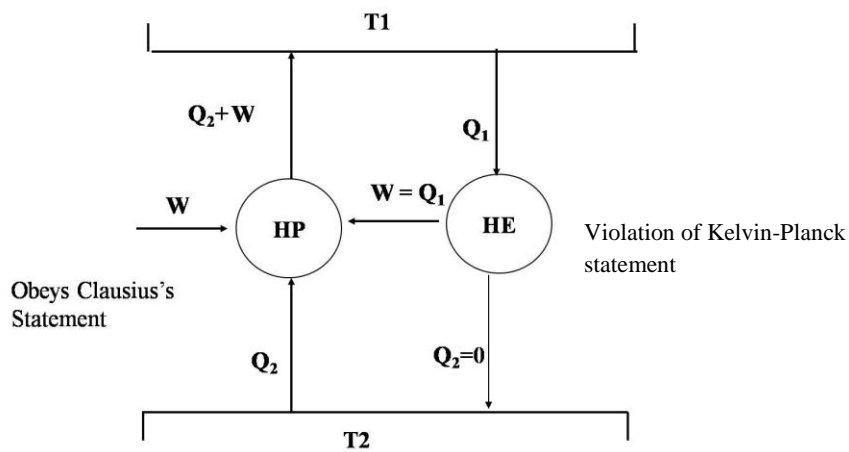


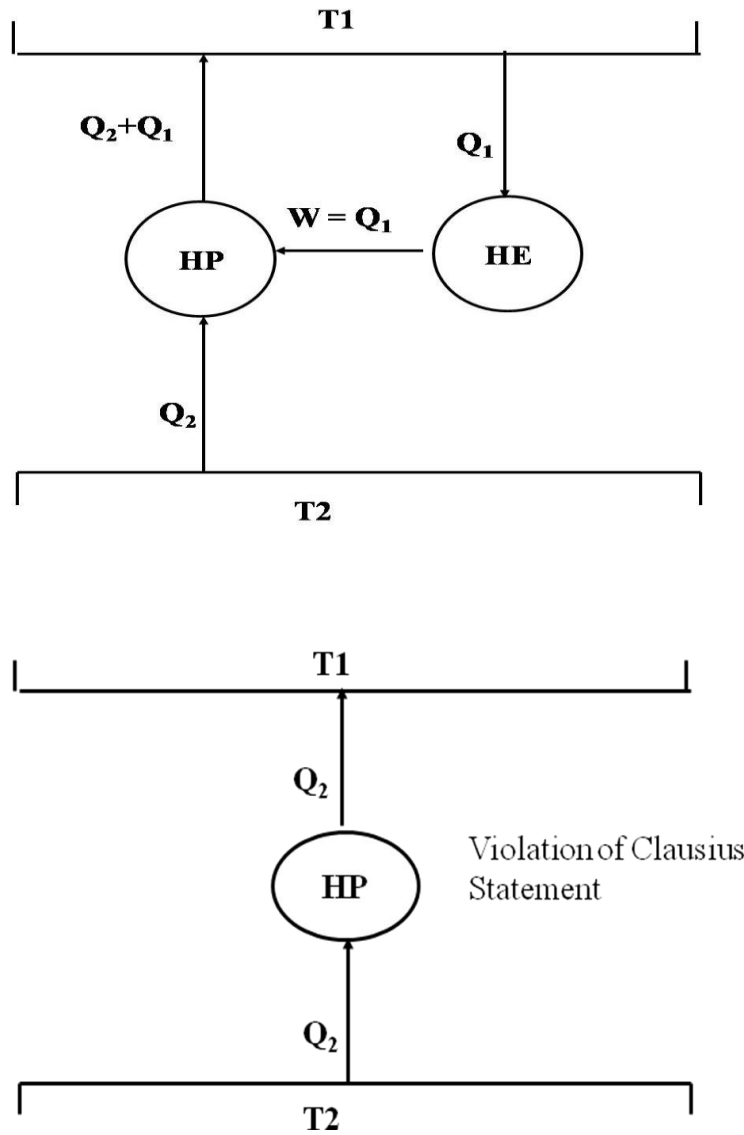
A refrigerator that violates the Clausius statement of the second law

Equivalence of Kelvin Planck and Clausius Statements:

The equivalence of the statement is demonstrated by showing that the violation of each statement implies the violation of other.

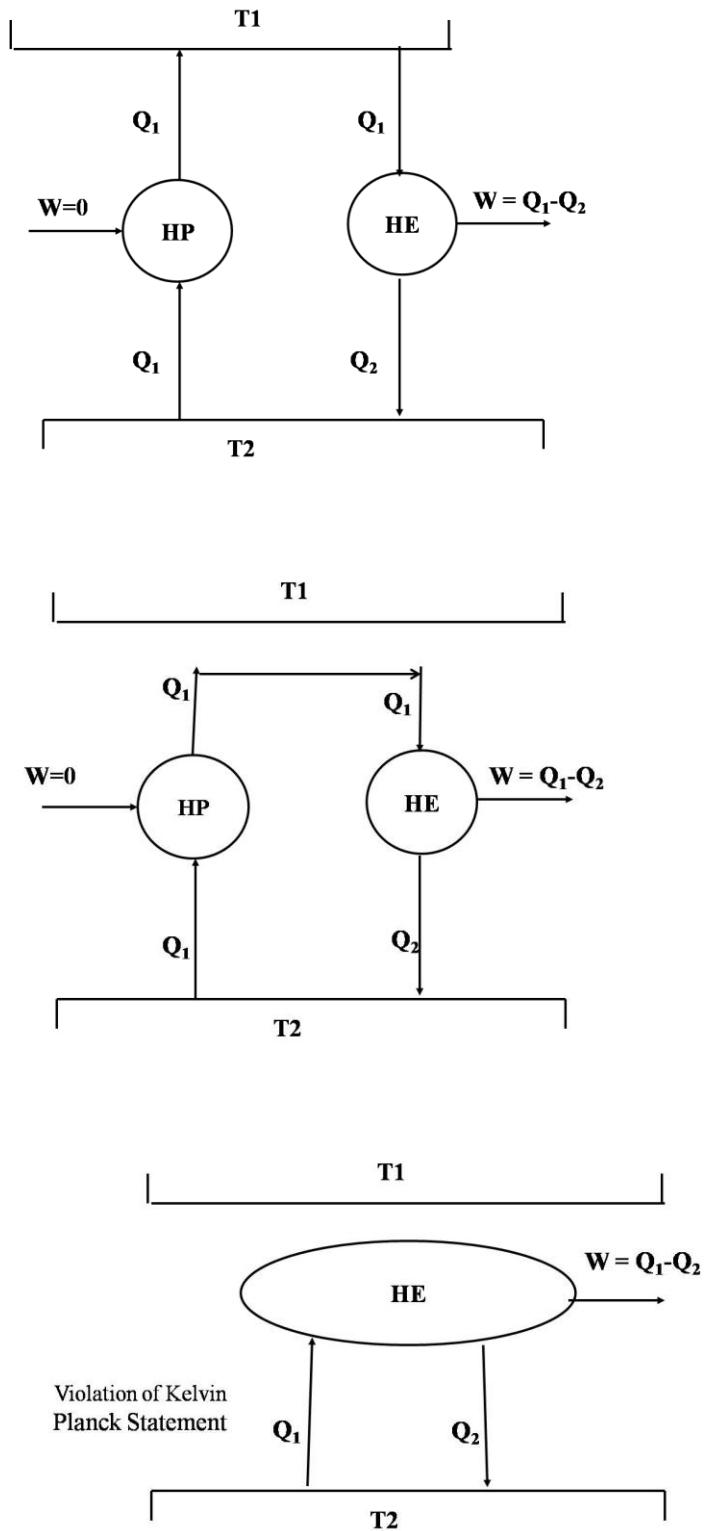
CASE-1: Violation of Kelvin-planck statement leads to violation of Clausius statement





Thus violation Kelvin Planck Statement has lead to the violation of Clausius Statement

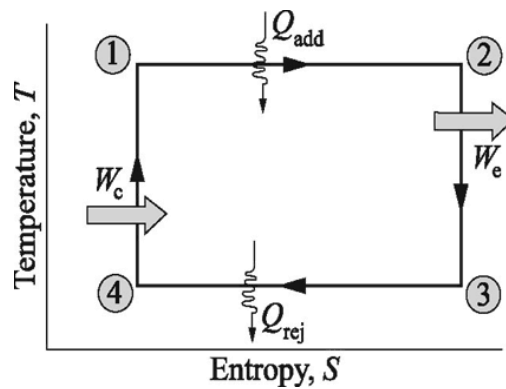
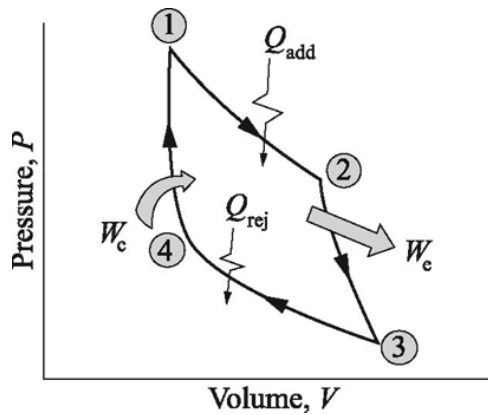
CASE-2: Violation of Clausius statement leads to violation of Kelvin-planck statement



Thus Violation of Clausius Statement has lead to violation of Kelvin Planck Statements

Carnot Cycle: Carnot cycle is a reversible cycle that is composed of four reversible processes, two isothermal and two adiabatic.

- **Process 1 - 2 (Reversible Isothermal Heat Addition)**
- **Process 2 - 3 (Reversible Adiabatic Expansion)**
- **Process 3 - 4 (Reversible Isothermal Heat Rejection)**
- **Process 4 - 1 (Reversible Adiabatic Compression)**



$$\Sigma(Q_{\text{net}})_{\text{cycle}} = \Sigma(W_{\text{net}})_{\text{cycle}}$$

$$Q_{\text{add}} - Q_{\text{rej}} = W_e - W_c$$

$$\eta = \frac{W_{\text{net}}}{Q_{\text{add}}} = \frac{Q_{\text{add}} - Q_{\text{rej}}}{Q_{\text{add}}}$$

$$\eta = 1 - \frac{Q_{\text{rej}}}{Q_{\text{add}}}$$

From T-S diagram

$$\eta = 1 - \frac{T_2 (\Delta S)}{T_1 (\Delta S)}$$

$$\eta = 1 - \frac{T_2}{T_1}$$

Carnot's Theorem:

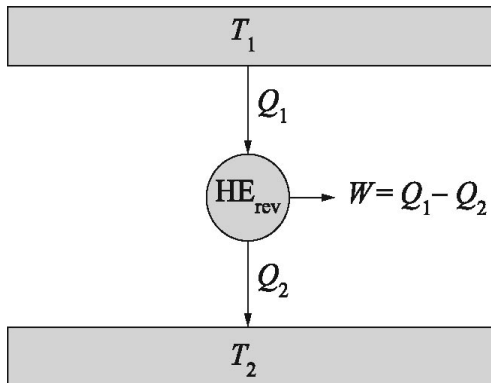
1. The efficiency of an irreversible heat engine is always less than efficiency of a reversible one operating between the same two reservoirs.
2. The efficiencies of all reversible heat engines operating between the same reservoirs are the same.

Clausius Inequality

The cyclic integral of $\frac{\delta Q}{T}$ is always less than or equal to zero.

Mathematically it can be expressed as $\oint \frac{\delta Q}{T} \leq 0$. The equality in the Clausius inequality holds for totally or just reversible cycle and the inequality for the irreversible ones.

Reversible Engine



$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

(or)

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0$$

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

For an Irreversible Engine

$$Q_1 - Q_{2I} < Q_1 - Q_{2R}$$

and therefore

$$Q_{2I} > Q_{2R}$$

Consequently, for an irreversible heat engine

$$\oint \delta Q = Q_1 - Q_{2I} > 0$$

$$\oint \frac{\delta Q}{T} = \frac{Q_1}{T_1} - \frac{Q_{2I}}{T_2} < 0$$

So we conclude that for all irreversible heat engine

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

Entropy:

Entropy is defined as $dS = \left(\frac{\delta Q}{T} \right)_{rev}$

The T ds Relations:

$$\delta Q_{rev} = dU + \delta W_{rev}$$

$$\text{But } \delta Q_{rev} = TdS$$

$$\text{and } \delta W_{rev} = PdV$$

Thus, The first TdS equation is obtained as

$$TdS = dU + PdV$$

The second TdS equation is obtained by using the definition of enthalpy $h = u + pv$.

$$dH = dU + d(PV) = dU + PdV + VdP$$

$$TdS = dH - VdP \quad (\text{Since } TdS = dU + PdV)$$

The TdS equations can be written on a unit mass basis as

$$Tds = du + PdV$$

$$Tds = dh - v dP$$

Entropy change of an ideal gas

The entropy change between two states of an ideal gas can be obtained from the ideal gas equation and the combined equation of the first and second laws.

$$Tds = du + PdV$$

But, $s_2 - s_1 = c_v \ln \left[\frac{T_2}{T_1} \right]$
 $du = c_v dT$ and $P = (RT)/v$

Therefore,

$$Tds = c_v dT + \left[\frac{RT}{v} \right] dv$$

or

$$\int_1^2 ds = \int_1^2 c_v \frac{dT}{T} + \int_1^2 R \frac{dv}{v}$$

$$\therefore s_2 - s_1 = c_v \ln \left[\frac{T_2}{T_1} \right] + R \ln \left[\frac{v_2}{v_1} \right]$$

Again, $Tds = dh - v dP$

Now,

$$dh = c_p dT \quad \text{and} \quad v = (RT)/P$$

$$ds = c_p \left[\frac{dT}{T} \right] - \left[\frac{RT}{PT} \right] dP$$

$$\int_1^2 ds = \int_1^2 c_p \frac{dT}{T} - R \int_1^2 \frac{dP}{P}$$

$$\therefore s_2 - s_1 = c_p \ln \left[\frac{T_2}{T_1} \right] - R \ln \left[\frac{P_2}{P_1} \right]$$

Entropy change for different process:

Process	Entropy change $s_2 - s_1$
Reversible constant volume process	$s_2 - s_1 = c_v \ln \left[\frac{T_2}{T_1} \right]$
Reversible constant pressure process	$s_2 - s_1 = c_p \ln \left[\frac{T_2}{T_1} \right]$