# Engineering Thermodynamics

***Second Law of Thermodynamics***

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## 5.1. LIMITATIONS OF FIRST LAW OF THERMODYNAMICS AND INTRODUCTION TO SECOND LAW

- It has been observed that *energy can flow* from a system in the form of *heat* or *work*.
- The first law of thermodynamics sets no limit to the amount of the total energy of a system which can be caused to flow out as work.
- A limit is imposed, however, as a result of the principle enunciated in the second law of thermodynamics which states that heat will flow naturally from one energy reservoir to another at a lower temperature, but not in opposite direction without assistance.



## 5.1. LIMITATIONS OF FIRST LAW OF THERMODYNAMICS AND INTRODUCTION TO SECOND LAW

- This is very important because a heat engine operates between two energy reservoirs at different temperatures.
- Further the first law of thermodynamics *establishes equivalence between the quantity of heat used and the mechanical work but does not specify the conditions under which conversion of heat into work is possible, neither the direction in which heat transfer can take place*.
- This gap has been *bridged* by the second law of thermodynamics.

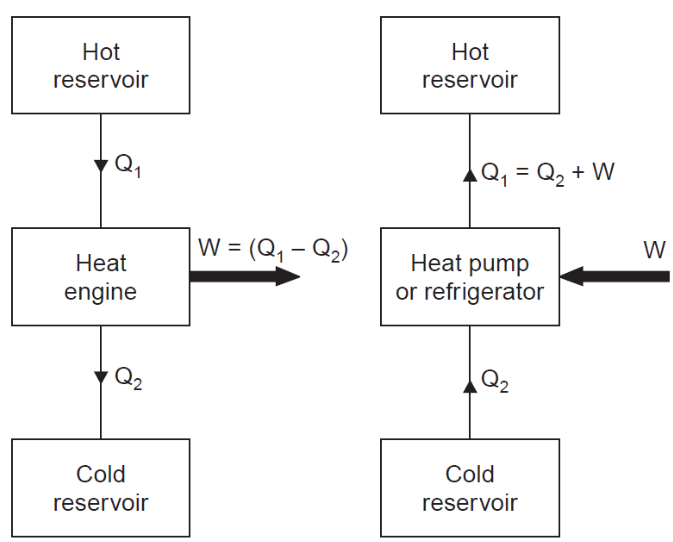


## 5.2. PERFORMANCE OF HEAT ENGINES AND REVERSED HEAT ENGINES

- Refer Fig. (*a*). A *heat engine* is used to produce the maximum work transfer from a given positive heat transfer.
- The measure of success is called the ***thermal efficiency*** of the engine and is defined by the ratio :

$$\text{Thermal efficiency, } \eta_{th} = \frac{W}{Q_1} \quad \text{...(5.1)}$$

$W$ = Net work transfer from the engine, and
$Q_1$ = Heat transfer to engine.




(a) Heat engine

(b) Heat pump or refrigerator

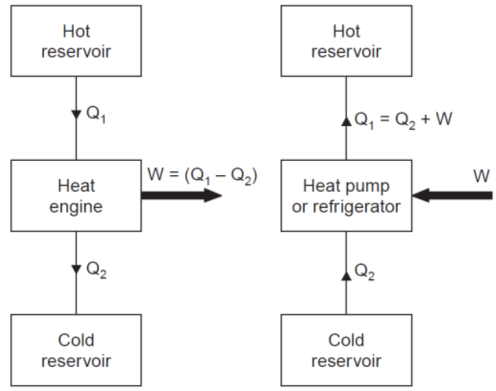
## 5.2. PERFORMANCE OF HEAT ENGINES AND REVERSED HEAT ENGINES

For a *reversed heat engine* [Fig. (*b*)] acting as a *refrigerator* when the purpose is to achieve the maximum heat transfer from the cold reservoir, the measure of success is called the ***co-efficient of performance*** (C.O.P.). It is defined by the ratio :

$$\text{Co-efficient of performance, } (\text{C.O.P.})_{ref.} = \frac{Q_2}{W} \qquad ...(5.2)$$

$Q_2$ = Heat transfer *from cold reservoir*, and

$W$ = The net work transfer to the refrigerator.




(a) Heat engine

(b) Heat pump or refrigerator



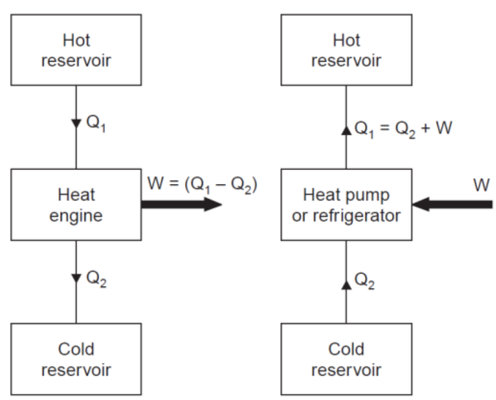
## 5.2. PERFORMANCE OF HEAT ENGINES AND REVERSED HEAT ENGINES

For a *reversed heat engine* [Fig. (*b*)] acting as a *heat pump*, the measure of success is again called the *co-efficient of performance*. It is defined by the ratio :

$$\text{Co-efficient of performance, } (\text{C.O.P.})_{heat\ pump} = \frac{Q_1}{W} \qquad ...(5.3)$$

$Q_1$ = Heat transfer *to hot reservoir*, and

$W$ = Net work transfer to the heat pump.




(a) Heat engine

(b) Heat pump or refrigerator

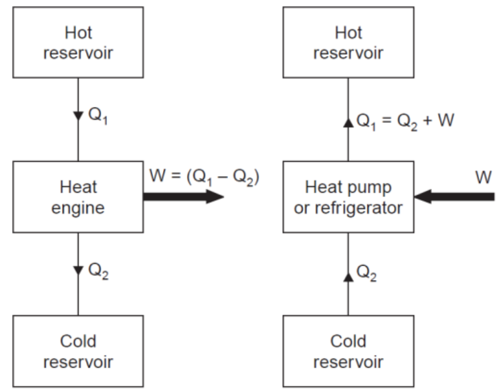
## 5.2. PERFORMANCE OF HEAT ENGINES AND REVERSED HEAT ENGINES

In all the above three cases application of the first law gives the relation $Q_1 - Q_2 = W$, and this can be used to rewrite the expressions for thermal efficiency and co-efficient of performance solely in terms of the heat transfers.

$$\eta_{th} = \frac{Q_1 - Q_2}{Q_1} \quad ..(5.4)$$

$$(C.O.P.)_{ref} = \frac{Q_2}{Q_1 - Q_2} \quad ...(5.5)$$

$$(C.O.P.)_{heat\ pump} = \frac{Q_1}{Q_1 - Q_2} \quad ..(5.6)$$



(a) Heat engine
(b) Heat pump or refrigerator

It may be seen that $\eta_{th}$ is *always less than unity* and $(C.O.P.)_{heat\ pump}$ is *always greater than unity*.



## 5.3. REVERSIBLE PROCESSES

- A reversible process should fulfill the following *conditions* :

1. The process should not involve friction of any kind.
2. Heat transfer should not take place with finite temperature difference.
3. The energy transfer as heat and work during the forward process should be identically equal to energy transfer as heat and work during the reversal of the process.
4. There should be no free or unrestricted expansion.
5. There should be no mixing of the fluids.
6. The process must proceed in a series of equilibrium states.

## 5.3. REVERSIBLE PROCESSES

- Some examples of ***ideal reversible processes*** are :

(*i*) Frictionless adiabatic expansion or compression;

(*ii*) Frictionless isothermal expansion or compression;

(*iii*) Condensation and boiling of liquids.

- Some examples of ***irreversible processes*** *are* :

(*i*) Combustion process; (*ii*) Mixing of two fluids;

(*iii*) All processes involving friction; (*iv*) Flow of electric current through a resistance;

(*v*) Heat flow from a higher temperature to lower temperature.

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## 5.3. REVERSIBLE PROCESSES

- *Reversible processes* are preferred because the devices which produce work such as engines and turbines, reversible process of the working fluid delivers *more work* than the corresponding irreversible processes.
- Also in case of fans, compressors, refrigerators and pumps *less power input* is required when *reversible processes* are used in place of corresponding irreversible ones.

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## 5.3. REVERSIBLE PROCESSES

- In thermodynamic analysis concept of reversibility, though hypothetical, is very important because a reversible process is the *most efficient process*. Only reversible processes can be truly represented on property diagrams.
- Thermodynamic reversibility can only be approached but can *never* be achieved.
- Thus the main task of the engineer is to design the system which will evolve approximate reversible processes.



## 5.4. STATEMENTS OF SECOND LAW OF THERMODYNAMICS

- The second law of thermodynamics has been enunciated meticulously by **Clausius**, **Kelvin** and **Planck** in slightly different words although both statements are basically identical.
- Each statement is based on an ***irreversible process***.
- The *first considers transformation of heat between two thermal reservoirs* while the *second considers the transformation of heat into work*.

## 5.4. STATEMENTS OF SECOND LAW OF THERMODYNAMICS

### 5.4.1. Clausius Statement

- *"It is impossible for a self acting machine working in a cyclic process unaided by any external agency, to convey heat from a body at a lower temperature to a body at a higher temperature"*.
- In other words, heat of, itself, cannot flow from a colder to a hotter body.

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## 5.4. STATEMENTS OF SECOND LAW OF THERMODYNAMICS

### 5.4.2. Kelvin-Planck Statement

- *"It is impossible to construct an engine, which while operating in a cycle produces no other effect except to extract heat from a single reservoir and do equivalent amount of work"*.
- Although the Clausius and Kelvin-Planck statements appear to be different, they are really equivalent in the sense that a *violation of either statement implies violation of other*.

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## 5.4. STATEMENTS OF SECOND LAW OF THERMODYNAMICS

### 5.4.3. Equivalence of Clausius Statement to the Kelvin-Planck Statement

- Refer Fig. 5.2. Consider a higher temperature reservoir $T_1$ and low temperature reservoir $T_2$.
- Fig. 5.2 shows a heat pump which requires no work and transfers an amount of $Q_2$ from a low temperature to a higher temperature reservoir (in violation of the Clausius statement).

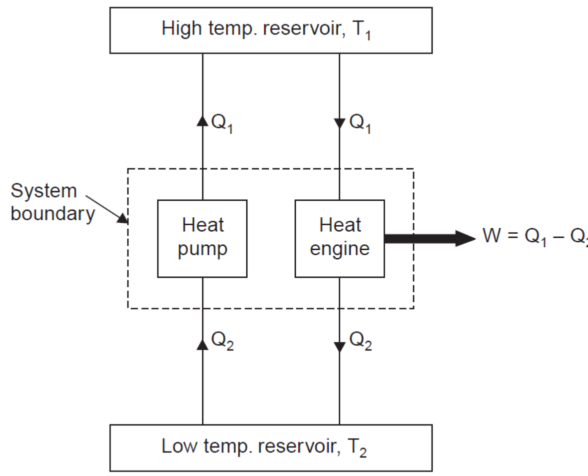


Fig. 5.2. Equivalence of Clausius statement to Kelvin-Planck statement.



## 5.4. STATEMENTS OF SECOND LAW OF THERMODYNAMICS

### 5.4.3. Equivalence of Clausius Statement to the Kelvin-Planck Statement

Let an amount of heat $Q_1$ (greater than $Q_2$) be transferred from high temperature reservoir to heat engine which devolops a net work, $W = Q_1 - Q_2$ and rejects $Q_2$ to the low temperature reservoir.

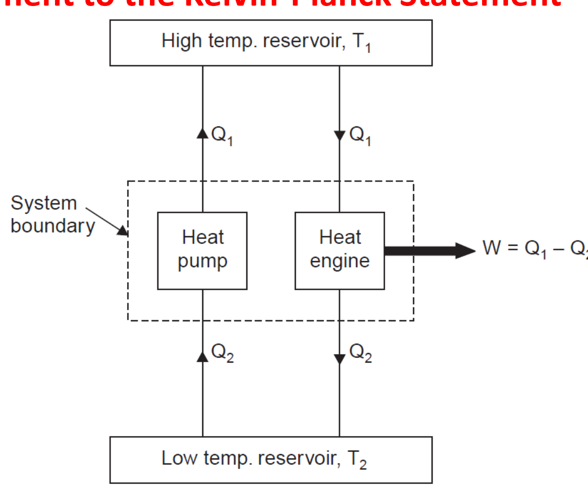


Fig. 5.2. Equivalence of Clausius statement to Kelvin-Planck statement.

## 5.4. STATEMENTS OF SECOND LAW OF THERMODYNAMICS

### 5.4.3. Equivalence of Clausius Statement to the Kelvin-Planck Statement

- Since there is no heat interaction with the low temperature, it can be eliminated.
- The combined system of the heat engine and heat pump acts then like a heat engine exchanging heat with a single reservoir, which is the violation of the Kelvin-Planck statement.

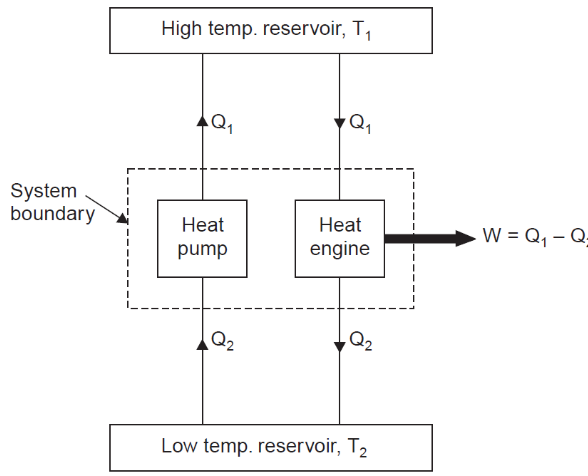


Fig. 5.2. Equivalence of Clausius statement to Kelvin-Planck statement.

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## 5.5. PERPETUAL MOTION MACHINE OF THE SECOND KIND

- ➢A machine which violates the first law of thermodynamics is called the perpetual motion machine of the **first kind** (PMM1). Such a machine creates its own energy from nothing and *does not exist*.
- ➢Without violating the first law, a machine can be imagined which would continuously absorb heat from a single thermal *reservoir and would convert this heat completely into work. The efficiency* of such a machine would be *100 per cent*. This machine is called the *perpetual motion machine of the **second kind** (PMM2)*.

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## 5.5. PERPETUAL MOTION MACHINE OF THE SECOND KIND

Fig. 5.3 shows the perpetual motion machine of the second kind. *A machine of this kind will evidently violates the second law of thermodynamics*.

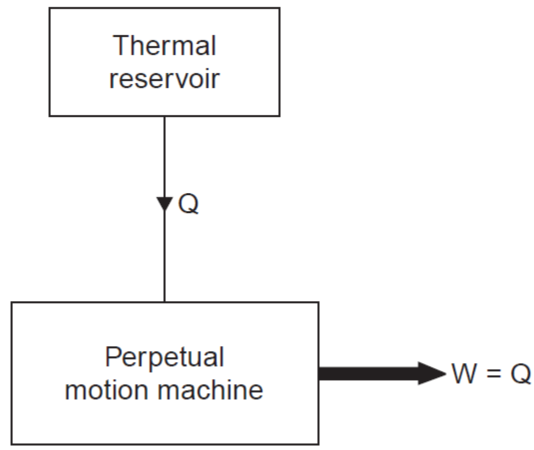


Fig. 5.3. Perpetual motion machine of second kind (PMM2).

## 5.6. THERMODYNAMIC TEMPERATURE

- Take the case of reversible heat engine operating between two reservoirs. Its thermal efficiency is given by the eqn. (5.4),

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

- The temperature of a reservoir remains uniform and fixed irrespective of heat transfer.
- This means that reservoir has only one property defining its state and the heat transfer from a reservoir is some function of that property, *temperature*.

## 5.6. THERMODYNAMIC TEMPERATURE

- Thus $Q = \phi(K)$, where $K$ is the temperature of reservoir.
- The choice of the function is universally accepted to be such that the relation,

$$\frac{Q_1}{Q_2} = \frac{\phi(K_1)}{\phi(K_2)} \text{ becomes } \frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad ...(5.7)$$

- where $T_1$ and $T_2$ are the thermodynamic temperatures of the reservoirs.

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## 5.6. THERMODYNAMIC TEMPERATURE

- Zero thermodynamic temperature (that temperature to which $T_2$ tends, as the heat transfer $Q_2$ tends to zero) has never been attained and *one form of third law of thermodynamics is the statement* :

**"The temperature of a system cannot be reduced to zero in a finite number of processes."**

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## 5.6. THERMODYNAMIC TEMPERATURE

- After establishing the concept of a zero thermodynamic temperature, a reference reservoir is chosen and assigned a numerical value of temperature.
- Any other thermodynamic temperature may now be defined in terms of reference value and the heat transfers that would occur with reversible engine,

$$T = T_{ref.} \frac{Q}{Q_{ref.}} \quad ...(5.8)$$

- The determination of thermodynamic temperature cannot be made in this way as it is not possible to build a reversible engine.



## 5.6. THERMODYNAMIC TEMPERATURE

- Temperatures are determined by the application of thermodynamic relations to other measurements.
- The SI unit of thermodynamic temperature is the kelvin (*K*).
- The relation between thermodynamic temperature and Celsius scale, which is in common use is :

Thermodynamic temperature = Celsius temperature + 273.15°.

- The kelvin unit of thermodynamic temperature is the fraction 1/273.15 of thermodynamic temperature of 'Triple point' of water.

## 5.7. CLAUSIUS INEQUALITY

- When a reversible engine uses more than two reservoirs the third or higher numbered reservoirs will not be equal in temperature to the original two.
- Consideration of expression for efficiency of the engine indicates that for maximum efficiency, all the heat transfer should take place at maximum or minimum reservoir temperatures.
- Any intermediate reservoir used will, therefore, lower the efficiency of the heat engine.
- Practical engine cycles often involve continuous changes of temperature during heat transfer.
- A relationship among processes in which these sort of changes occur is necessary.



## 5.7. CLAUSIUS INEQUALITY

- The ideal approach to a cycle in which temperature continually changes is to consider the system to be in communication with a large number of reservoirs in procession.
- Each reservoir is considered to have a temperature differing by a small amount from the previous one.
- In such a model it is possible to imagine that each reservoir is replaced by a reversible heat engine in communication with standard reservoirs at same temperature $T_0$.
- Fig. 5.4 shows one example to this substitution.

## 5.7. CLAUSIUS INEQUALITY

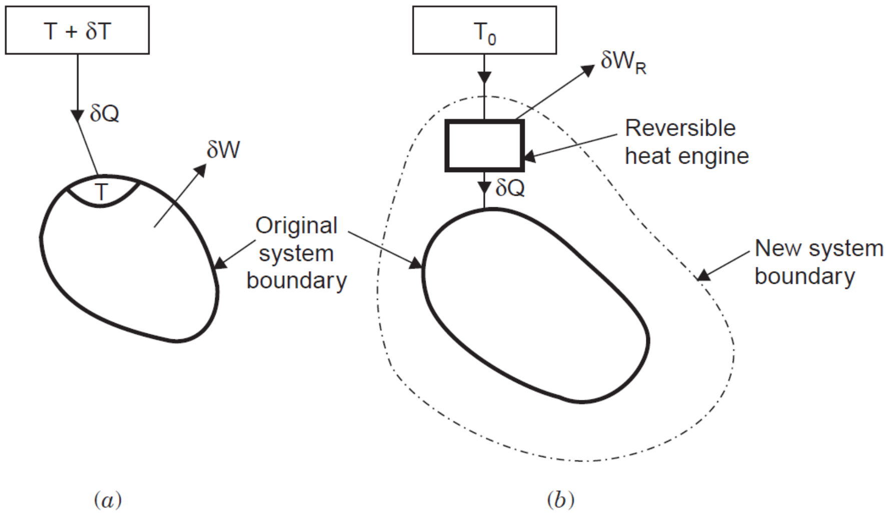


Fig. 5.4. The clausius inequality.

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## 5.7. CLAUSIUS INEQUALITY

- The system to which the heat transfer is effected is neither concerned with the source of energy it receives nor with the method of transfer, save that it must be reversible.
- Associated with the small heat transfer *dQ* to the original system is a small work transfer *dW* and for this system the first law gives

$$\sum_{\text{cycle}} (\delta Q - \delta W) = 0 \quad \text{...(5.9)}$$

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## 5.7. CLAUSIUS INEQUALITY

- Now consider the engine replacing the reservoirs and apply the second law to the new system in Fig. 5.4 (*b*).
- If the new system is not a perpetual motion machine of second kind, no positive work transfer is possible with a single reservoir.

Therefore, $$\sum_{\text{cycle}} (\delta W - \delta W_R) \leq 0 \qquad \text{...(5.10)}$$

- But by the definition of thermodynamic temperature in equation (5.8)

$$\frac{\delta W_R}{\delta Q} = \frac{\delta Q_0 - \delta Q}{\delta Q} = \frac{T_0 - T}{T} \qquad \text{...(5.11)}$$

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$$\sum_{\text{cycle}} (\delta Q - \delta W) = 0 \qquad \text{...(5.9)}$$

$$\sum_{\text{cycle}} (\delta W - \delta W_R) \leq 0 \qquad \text{...(5.10)}$$

$$\frac{\delta W_R}{\delta Q} = \frac{\delta Q_0 - \delta Q}{\delta Q} = \frac{T_0 - T}{T} \qquad \text{...(5.11)}$$

## 5.7. CLAUSIUS INEQUALITY

- and by combination of eqns. (5.9), (5.10) and (5.11)

$$T_0 \sum_{\text{cycle}} \left(\frac{\delta Q}{T}\right) \leq 0 \text{ but } T_0 \neq 0 \text{ and therefore ;}$$

$$\sum_{\text{cycle}} \left(\frac{\delta Q}{T}\right) \leq 0 \qquad \text{..(5.12)}$$

- This is known as **Clausius inequality**.

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## 5.7. CLAUSIUS INEQUALITY

- Let us now consider the case of a reversible engine for which

$$\sum_{\text{cycle}} \left(\frac{\delta Q}{T}\right) \leq 0 \ ,$$

reverse the engine and for the reversible heat pump obtained it is possible to develop the expression,

$$-\sum_{\text{cycle}} \left(\frac{\delta Q}{T}\right) \leq 0$$

- The *negative sign indicates that the heat transfers have all reversed in direction when the engine was reversed*. This means that for the same machine we have two relations which are only satisfied if in the reversible case,

$$\sum_{\text{cycle}} \left(\frac{\delta Q}{T}\right) \leq 0 \quad \ldots(5.13)$$



## 5.7. CLAUSIUS INEQUALITY

- For a reversible case, as the number of reservoirs used tends to infinity, the limiting value of the summation will be

$$\sum_{\text{cycle}} \left(\frac{\delta Q}{T}\right) = 0$$

- In words, the Clausius inequality may be expressed as follows :

*"When a system performs a reversible cycle, then*

$$\sum_{\text{cycle}} \left(\frac{\delta Q}{T}\right) = 0,$$

*but when the cycle is not reversible*

$$\sum_{\text{cycle}} \left(\frac{\delta Q}{T}\right) < 0 \text{"}.$$